

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problems Mailbox.**

428-408

SR

2/20/79

XR 4,140,832

# United States Patent [19]

Menegay

[11] 4,140,832

[45] Feb. 20, 1979

[54] ELECTROMOTIVE BRUSHES PRODUCED  
FROM MESOPHASE PITCH FIBERS

[75] Inventor: Daniel J. Menegay, Olmstead  
Township, Cuyahoga County, Ohio

[73] Assignee: Union Carbide Corporation, New  
York, N.Y.

[21] Appl. No.: 753,810

[22] Filed: Dec. 23, 1976

[51] Int. Cl.<sup>2</sup> ..... H01R 39/26  
[52] U.S. Cl. ..... 428/288; 310/248;  
310/253; 427/114; 428/290; 428/408; 428/902  
[58] Field of Search ..... 310/251, 252, 253, 248;  
427/114; 264/176 F; 428/290, 408, 902

[56] References Cited

U.S. PATENT DOCUMENTS

2,224,724	12/1940	Elsey .....	427/114
3,108,018	10/1963	Lewis .....	428/408
3,165,480	1/1965	Churchill .....	310/253
3,367,812	2/1968	Watts .....	156/155
3,406,126	10/1968	Litant .....	252/511
3,751,294	8/1973	Fredman et al. ....	310/253
3,829,327	8/1974	Omori et al. ....	423/447
3,960,601	6/1976	Schultz .....	136/122
3,976,729	8/1976	Lewis et al. ....	264/176 F
3,996,048	12/1976	Fredman et al. ....	427/385 R
4,032,607	6/1977	Schultz .....	156/148

Primary Examiner—James J. Bell

Attorney, Agent, or Firm—John S. Piscitello

[57] ABSTRACT

Electromotive brushes having improved commutating properties composed of a dense, rigid plate of self-

bonded, non-woven carbon fibers formed from mesophase pitch fibers. The brushes are produced by spinning a mesophase pitch to form carbonaceous pitch fiber; disposing staple lengths of the spun fiber in intimately contacting relationship with each other in a non-woven fibrous web; heating the web produced in this manner in an oxidizing atmosphere to thermoset the surfaces of the fibers to an extent which will allow the fibers to maintain their shape upon heating to more elevated temperatures but insufficient to thermoset the pitch in the interior portions of the fibers to an extent which will prevent the pitch from flowing and exuding through surface pores or flaws in the fibers when the web is further heated to more elevated temperatures under compressive pressure; further heating the web containing the externally thermoset fibers under compressive pressure in an oxygen-free atmosphere to a temperature sufficiently elevated to cause the mesophase pitch in the unoxidized interior portions of the fibers to undergo liquid flow and exude through surface pores or flaws in the fibers and contact the surfaces of the adjacent fibers; continuing to heat the web in an oxygen-free atmosphere to a carbonizing temperature so as to expel hydrogen and other volatiles and produce a dense, rigid carbon body wherein the fibers are bonded to each other by infusible carbon bonds; optionally, further heating the carbon body to a graphitizing temperature in an oxygen-free atmosphere; and then impregnating the carbonized or graphitized body with a thermosetting resin and heating it at a temperature sufficiently elevated to cure the resin impregnant.

3 Claims, No Drawings

**ELECTROMOTIVE BRUSHES PRODUCED FROM  
MESOPHASE PITCH FIBERS**

**BACKGROUND OF THE INVENTION**

This invention relates to novel electromotive brushes having improved commutating properties.

Electromotive brushes have conventionally been made with lampblack base electrographite. As the operating conditions of motors and generators have become more demanding, however, a need has developed for electromotive brushes possessing improved commutation properties. Significant improvement in such properties have been attained with the advent of flexible brushes formed with carbon fibers. However, flexible brushes of this kind require an elaborate construction wherein the fiber ends are electroplated and held together by means of a metal container. Such construction not only significantly increases the cost of the brush, but also leaves a shortened brush length available for wear. In addition, such brushes exhibit unsatisfactory high friction and high contact drops when in operation, which cause undesirable heating effects and shorter brush life.

**SUMMARY OF THE INVENTION**

In accordance with the present invention, it has now been discovered that highly conductive, low cost, dense, rigid plates composed of self-bonded non-woven carbon fibers, and useful as electromotive brushes, can be produced by spinning a carbonaceous pitch having a mesophase content of from about 40 per cent by weight to about 90 per cent by weight to form carbonaceous pitch fiber; disposing staple lengths of the spun fiber in an intimate relationship with each other in a non-woven fibrous web; heating the web produced in this manner in an oxidizing atmosphere to thermoset the surfaces of the fibers to an extent which will allow the fibers to maintain their shape upon heating to more elevated temperatures but insufficient to thermoset the pitch in the interior portions of the fibers to an extent which will prevent the pitch from flowing and exuding through surface pores or flaws in the fibers when the web is further heated to more elevated temperatures under compressive pressure; further heating the web containing the externally thermoset fibers under compressive pressure in an oxygen-free atmosphere to a temperature sufficiently elevated to cause the mesophase pitch in the unoxidized interior portions of the fibers to undergo liquid flow and exude through surface pores or flaws in the fibers and contact the surfaces of the adjacent fibers; continuing to heat the web in an oxygen-free atmosphere to a carbonizing temperature so as to expel hydrogen and other volatiles and produce a dense, rigid carbon body wherein the fibers are bonded to each other by infusible carbon bonds; optionally further heating the carbon body to a graphitizing temperature in an oxygen-free atmosphere; and then impregnating the carbonized or graphitized body with a thermosetting resin and heating it at a temperature sufficiently elevated to cure the resin impregnant.

Electromotive brushes produced in this manner are characterized by high electrical anisotropy (greater than 8:1 up to in excess of 40:1) which helps impart to these materials their improved commutating properties. As a result, such brushes exhibit a higher current-carrying capacity and operate at a commutation latitude considerably higher than standard lampblack base elec-

trographitic brushes. At the same time, the brushes of the present invention do not exhibit the high friction and high contact drops characteristic of flexible carbon fiber brushes. Furthermore, because the fibers are self-bonded, essentially the entire brush is available for wear, as in conventional brushes. In addition, the life of such brushes has been found to be superior to the life of both conventional brushes and flexible carbon fiber brushes.

**DESCRIPTION OF THE PREFERRED  
EMBODIMENTS**

While carbonaceous fibers can be spun from non-mesophase pitches, only mesophase pitches are employed in the present invention because of their ability to produce highly-oriented fibers which can be easily thermoset. Mesophase pitches are pitches which have been transformed, in whole or in part, to a liquid crystal or so-called "mesophase" state. Such pitches by nature contain highly oriented molecules, and when these pitches are spun into fibers, the pitch molecules are preferentially aligned by the spinning process along the longitudinal axis of the fiber to produce a highly oriented fiber.

Mesophase pitches can be produced in accordance with known techniques by heating a natural or synthetic carbonaceous pitch having an aromatic base in an inert atmosphere at a temperature about 350° C. for a time sufficient to produce the desired quantity of mesophase. When such a pitch is heated in this manner under quiescent conditions, either at constant temperature or with gradually increasing temperature, small insoluble liquid spheres begin to appear in the pitch which gradually increase in size as heating is continued. When examined by electron diffraction and polarized light techniques, these spheres are shown to consist of layers of oriented molecules aligned in the same direction. As these spheres continue to grow in size as heating is continued, they come in contact with one another and gradually coalesce with each other to produce larger masses of aligned layers. As coalescence continues, domains of aligned molecules much larger than those of the original spheres are formed. These domains come together to form a bulk mesophase wherein the transition from one oriented domain to another sometimes occurs smoothly and continuously through gradually curving lamellae and sometimes through more sharply curving lamellae. The differences in orientation between the domains create a complex array of polarized light extinction contours in the bulk mesophase corresponding to various types of linear discontinuity in molecular alignment. The ultimate size of the oriented domains produced is dependent upon the viscosity, and the rate of increase of the viscosity, of the mesophase from which they are formed, which, in turn are dependent upon the particular pitch and the heating rate. In certain pitches domains having sizes in excess of two hundred microns and as large as several thousand microns are produced. In other pitches, the viscosity of the mesophase is such that only limited coalescence and structural rearrangement of layers occur, so that the ultimate domain size does not exceed one hundred microns.

The highly oriented, optically anisotropic, insoluble material produced by treating pitches in this manner has been given the term "mesophase", and pitches containing such material are known as "mesophase pitches". Such pitches, when heated above their softening points, are mixtures of two immiscible liquids, one the optically

anisotropic, oriented mesophase portion, and the other the isotropic non-mesophase portion. The term "mesophase" is derived from the Greek "mesos" or "intermediate" and indicates the pseudo-crystalline nature of this highly-oriented, optically anisotropic material.

Carbonaceous pitches having a mesophase content of from about 40 percent by weight to about 90 percent by weight are suitable for producing the highly oriented carbonaceous fibers from which the self-bonded webs employed in the present invention can be produced. In order to obtain the desired fibers from such pitch, however, the mesophase contained therein must, under quiescent conditions, form a homogeneous bulk mesophase having large coalesced domains, i.e., domains of aligned molecules in excess of two hundred microns. Pitches which form stringy bulk mesophase under quiescent conditions, having small oriented domains, rather than large coalesced domains, are unsuitable. Such pitches form mesophase having a high viscosity which undergoes only limited coalescence, insufficient to produce large coalesced domains having sizes in excess of two hundred microns. Instead, small oriented domains of mesophase agglomerate to produce clumps or stringy masses wherein the ultimate domain size does not exceed one hundred microns. Certain pitches which polymerize very rapidly are of this type. Likewise, pitches which do not form a homogeneous bulk mesophase are unsuitable. The latter phenomenon is caused by the presence of infusible solids (which are either present in the original pitch or which develop on heating) which are enveloped by the coalescing mesophase and serve to interrupt the homogeneity and uniformity of the coalesced domains, and the boundaries between them.

Another requirement is that the pitch be nonthixotropic under the conditions employed in the spinning of the pitch into fibers, i.e., it must exhibit a Newtonian or plastic flow behavior so that the flow is uniform and well behaved. When such pitches are heated to a temperature where they exhibit a viscosity of from about 10 poises to about 200 poises, uniform fibers may be readily spun therefrom. Pitches, on the other hand, which do not exhibit Newtonian or plastic flow behavior at the temperature of spinning, do not permit uniform fibers to be spun therefrom.

Carbonaceous pitches having a mesophase content of from about 40 percent by weight to about 90 percent by weight can be produced in accordance with known techniques, as aforesaid, by heating a natural or synthetic carbonaceous pitch having an aromatic base in an inert atmosphere at a temperature above about 350° C. for a time sufficient to produce the desired quantity of mesophase. By an inert atmosphere is meant an atmosphere which does not react with the pitch under the heating conditions employed, such as nitrogen, argon, xenon, helium, and the like. The heating period required to produce the desired mesophase content varies with the particular pitch and temperature employed, with longer heating periods required at lower temperatures than at higher temperatures. At 350° C., the minimum temperature generally required to produce mesophase, at least one week of heating is usually necessary to produce a mesophase content of about 40 percent. At temperatures of from about 400° C. to 450° C., conversion to mesophase proceeds more rapidly, and a 50 percent mesophase content can usually be produced at such temperatures within about 1-40 hours. Such temperatures are preferred for this reason. Temperatures above about 500° C. are undesirable, and heating at this tem-

perature should not be employed for more than about 5 minutes to avoid conversion of the pitch to coke.

The degree to which the pitch has been converted to mesophase can readily be determined by polarized light microscopy and solubility examinations. Except for certain non-mesophase insolubles present in the original pitch or which, in some instances, develop on heating, the non-mesophase portion of the pitch is readily soluble in organic solvents such as quinoline and pyridine, while the mesophase portion is essentially insoluble.<sup>(1)</sup> In the case of pitches which do not develop non-mesophase insolubles when heated, the insoluble content of the heat treated pitch over and above the insoluble content of the pitch before it has been heat treated corresponds essentially to the mesophase content.<sup>(2)</sup> In the case of pitches which do develop non-mesophase insolubles when heated, the insoluble content of the heat treated pitch over and above the insoluble content of the pitch before it has been heat treated is not solely due to the conversion of the pitch to mesophase, but also represents non-mesophase insolubles which are produced along with the mesophase during the heat treatment. Pitches which contain infusible non-mesophase insolubles (either present in the original pitch or developed by heating) in amounts sufficient to prevent the development of homogeneous bulk mesophase are unsuitable for producing highly oriented carbonaceous fibers useful in the present invention, as noted above. Generally, pitches which contain an excess of about 2 percent by weight of such infusible materials are unsuitable. The presence of absence of such homogeneous bulk mesophase regions, as well as the presence or absence of infusible non-mesophase insolubles, can be visually observed by polarized light microscopy examination of the pitch (see, e.g., Brooks, J. D., and Taylor, G. H., "The Formation of Some Graphitizing Carbons," Chemistry and Physics of Carbon, Vol. 4, Marcel Dekker, Inc., New York, 1968, pp. 243-268; and Dubois, J., Agache, C., and White, J. L., "The Carbonaceous Mesophase Formed in the Pyrolysis of Graphitizable Organic Materials," Metallography 3, pp. 337-369, 1970). The amounts of each of these materials may also be visually estimated in this manner.

(1) The percent of quinoline insolubles (Q.I.) of a given pitch is determined by quinoline extraction at 75° C. The percent of pyridine insolubles (P.I.) is determined by Soxhlet extraction in boiling pyridine (115° C.).

(2) The insoluble content of the untreated pitch is generally less than 1 percent (except for certain coal tar pitches) and consists largely of coke and carbon black found in the original pitch.

Aromatic base carbonaceous pitches having a carbon content of from about 92 percent by weight to about 96 percent by weight and a hydrogen content of from about 4 percent by weight to about 8 percent by weight are generally suitable for producing mesophase pitches which can be employed to produce the fibers useful in the instant invention. Elements other than carbon and hydrogen, such as oxygen, sulfur and nitrogen, are undesirable and should not be present in excess of about 4 percent by weight. When such extraneous elements are present in amounts of from about 0.5 percent by weight to about 4 percent by weight, the pitches generally have a carbon content of from about 92-95 percent by weight, the balance being hydrogen.

Petroleum pitch, coal tar pitch and acenaphthylene pitch are preferred starting materials for producing the mesophase pitches which are employed to produce the fibers useful in the instant invention. Petroleum pitch can be derived from the thermal or catalytic cracking of petroleum fractions. Coal tar pitch is similarly obtained

by the destructive distillation of coal. Both of these materials are commercially available natural pitches in which mesophase can easily be produced, and are preferred for this reason. Acenaphthylene pitch, on the other hand, is a synthetic pitch which is preferred because of its ability to produce excellent fibers. Acenaphthylene pitch can be produced by the pyrolysis of polymers of acenaphthylene as described by Edstrom et al. in U.S. Pat. No. 3,574,653.

Some pitches, such as flouanthene pitch, polymerize very rapidly when heated and fail to develop large coalesced domains of mesophase, and are, therefore, not suitable precursor materials. Likewise, pitches having a high infusible non-mesophase insoluble content in organic solvents such as quinoline or pyridine, or those which develop a high infusible non-mesophase insoluble content when heated, should not be employed as starting materials, as explained above, because these pitches are incapable of developing the homogeneous bulk mesophase necessary to produce highly oriented carbonaceous fibers. For this reason, pitches having an infusible quinoline-insoluble or pyridine-insoluble content of more than about 2 percent by weight (determined as described above) should not be employed, or should be filtered to remove this material before being heated to produce mesophase. Preferably, such pitches are filtered when they contain more than about 1 percent by weight of such infusible, insoluble material. Most petroleum and synthetic pitches have a low infusible, insoluble content and can be used directly without such filtration. Most coal tar pitches, on the other hand, have a high infusible, insoluble content and require filtration before they can be employed.

As the pitch is heated at a temperature between 350° C. and 500° C. to produce mesophase, the pitch will, of course, pyrolyze to a certain extent and the composition of the pitch will be altered, depending upon the temperature, the heating time, and the composition and structure of the starting material. Generally, however, after heating a carbonaceous pitch for a time sufficient to produce a mesophase content of from about 40 percent by weight to about 90 percent by weight, the resulting pitch will contain a carbon content of from about 94-96 percent by weight and a hydrogen content of from about 4-6 percent by weight. When such pitches contain elements other than carbon and hydrogen in amounts of from about 0.5 percent by weight to about 4 percent by weight, the mesophase pitch will generally have a carbon content of from about 92-95 percent by weight, the balance being hydrogen.

After the desired mesophase pitch has been prepared, it is spun into fiber by conventional techniques, e.g., by melt spinning, centrifugal spinning, blow spinning, or in any other known manner. As noted above, in order to obtain highly oriented carbonaceous fibers from which the self-bonded webs employed in the present invention can be produced the pitch must, under quiescent conditions, form a homogeneous bulk mesophase having large coalesced domains, and be nonthixotropic under the conditions employed in the spinning. Further, in order to obtain uniform fibers from such pitch, the pitch should be agitated immediately prior to spinning so as to effectively intermix the immiscible mesophase and non-mesophase portions of the pitch.

The temperature at which the pitch is spun depends, of course, upon the temperature at which the pitch exhibits a suitable viscosity, and at which the higher-melting mesophase portion of the pitch can be easily

deformed and oriented. Since the softening temperature of the pitch, and its viscosity at a given temperature, increases as the mesophase content of the pitch increases, the mesophase content should not be permitted to rise to a point which raises the softening point of the pitch to excessive levels. For this reason, pitches having a mesophase content of more than about 90 percent are generally not employed. Pitches containing a mesophase content of from about 40 percent by weight to about 90 percent by weight, however, generally exhibit a viscosity of from about 10 poises to about 200 poises at temperatures of from about 310° C. to above about 450° C. and can be readily spun at such temperatures. Preferably, the pitch employed has a mesophase content of from about 45 percent by weight to about 75 percent by weight, most preferably from about 55 percent by weight to about 75 percent by weight, and exhibits a viscosity of from about 30 poises to about 150 poises at temperatures of from about 340° C. to about 440° C. At such viscosity and temperature, uniform fibers having diameters of from about 5 microns to about 25 microns can be easily spun. As previously mentioned, however, in order to obtain the desired fibers, it is important that the pitch be nonthixotropic and exhibit Newtonian or plastic flow behavior during the spinning of the fibers.

The carbonaceous fibers produced in this manner are highly-oriented materials having a high degree of preferred orientation of their molecules parallel to the fibers axis, as shown by their X-ray diffraction patterns. This preferred orientation is apparent from the short arcs which constitute the (002) bands of the diffraction pattern. Microdensitometer scanning of the (002) bands of the exposed X-ray film indicate this preferred orientation to be generally from about 20° to about 35°, usually from about 25° to about 30° (expressed as the full width at half maximum of the azimuthal intensity distribution).

After the fiber has been spun, staple lengths of the fiber are formed into a non-woven web wherein the staple fiber lengths are disposed in intimately contacting relationship with each other. Preferably the staple lengths are produced by blow-spinning of the pitch, and the blow-spun fibers are disposed into a web directly from the spinnerette. This can be conveniently accomplished by positioning a screen in the vicinity of the spinnerette and reducing the pressure behind the screen so as to draw the blow-spun fibers onto the screen. The fibers are preferably deposited on the screen so as to produce a web having an areal density of about 0.05 - 0.5 kg./m<sup>2</sup> of screen surface. The screen employed is preferably in the form of an endless wire mesh conveyor belt which can be used to transport the web through an oxidizing atmosphere.

Alternatively, continuous fiber can be spun and then cut or chopped into a desired length before being processed to form a web. Any method, either wet or dry, which effects the disposition of such fibers in intimately contacting relation in a non-woven fibrous web can be employed. Air laying operations, such as carding or garnetting, which effect a relatively oriented disposition of fibers are suitable for this purpose. When a more random disposition of fibers is desired, conventional textile devices which effect the air laying of fibers in a random webbing can be employed.

The fibers can also be formed into a web by water laying the fibers using conventional paper making techniques. When such techniques are employed, the fibers are first cut to a length suitable for processing, e.g.,

about  $\frac{1}{4}$  inch in length, homogeneously intermixed with water and a suitable binder, such as starch or other well known binder, to form an aqueous slurry, and then deposited from the slurry on a substrate to form a web. Generally, the web is formed either by running a dilute suspension of fibers onto the surface of a moving endless belt of wire cloth, through which excess water may be drawn, or by running an endless belt of wire cloth through a suspension of the fibers. In the first case, a part of the water is drawn off by gravity, a part is taken from the web by suction, and a part is removed by pressure. In the second case, a vacuum is maintained below the stock level in the cylinder in which the wire cloth is rotating and the web forms on the wire by suction. In either case, the thickness of the web is controlled by the speed of the conveyor belt, by the consistency of the fiber suspension, and by the amount of suspension permitted to flow onto the belt.

After the non-woven fibrous web has been formed, it is heated in an oxidizing atmosphere for a time sufficient to thermoset the surfaces of the fibers of the web to an extent which will allow the fibers to maintain their shape upon heating to more elevated temperatures but insufficient to thermoset the pitch in the interior portions of the fibers to an extent which will prevent the pitch from flowing and exuding through surface pores or flaws in the fibers when the web is further heated to more elevated temperatures under compressive pressure. Generally, thermosetting the fibers to an oxygen content of at least 1 percent by weight is necessary to allow them to maintain their shape upon heating to more elevated temperatures. Thermosetting can be continued up to an oxygen level of 12 percent without interrupting satisfactory flow of the pitch in the interior portions of the fibers upon further heating at more elevated temperatures, provides sufficient compressive pressure is applied to the web during such heating. When the web is so heated at more elevated temperatures, small droplets of molten pitch exude from the fibers at intervals along the fiber lengths and contact the surfaces of the adjacent fibers. The pressure applied to the web during such heating serves to compact the fibers and utilizes this bleeding to bond the fibers together into a dense, rigid, cohesive, self-bonded, mass. Upon further heating to a carbonizing temperature in an oxygen-free atmosphere so as to expel hydrogen and other volatiles, infusible carbon bonds are produced between the fibers.

As noted above, the non-woven fibrous web is preferably produced by blow-spinning staple lengths of fiber and collecting the blow-spun fibers on an endless wire mesh conveyor belt which can be used to transport the web through an oxidizing atmosphere. By varying the speed of this belt it is possible to expose the web to the oxidizing atmosphere for any desired length of time and thereby thermoset the fibers contained therein to any desired degree. The extent to which the fibers are oxidized, of course, will determine the degree to which they will bleed when heated to a temperature sufficiently elevated to cause the mesophase pitch in the unoxidized interior portions of the fibers to undergo liquid flow, i.e., the degree to which the pitch will exude through surface pores or flaws in the fibers. If desired, an oxidizing oven containing a number of zones having progressively higher temperature can be employed so as to allow the fibers to be gradually heated to the desired final oxidizing temperature. Because the oxidation reaction is an exothermic one, and hence

difficult to control, the oven is suitably a convection oven in which the oxidizing atmosphere may be passed through the web and wire mesh conveyor belt so as to remove heat of reaction from the immediate vicinity of the fibers and maintain a more constant temperature. The oxidizing gas, of course, may be recirculated through the oven after passing through the web and conveyor belt. To help maintain the web securely against the belt and prevent the fibers from blowing around in the oven, the oxidizing gas should be circulated downward through the web and belt rather than upward. The rate of flow of the gas, as well as the temperature, should be independently controlled in each zone of the oven to allow temperature and gas flow through the web to be regulated as desired. Gas velocity through the web is suitably maintained at a rate of from about 0.3 to about 3 meters per minute. The temperature of the zones is maintained, e.g., at from about 175° C. in the first or entrance zone up to about 400° C. in the last or exit zone.

The oxidizing atmosphere employed to thermoset the fibers of the non-woven webs employed in the present invention may be pure oxygen, nitric oxide, or any other appropriate oxidizing atmosphere. Most conveniently, air is employed as the oxidizing atmosphere.

The time required to thermoset the surface of the fibers will, of course, vary with such factors as the particular oxidizing atmosphere, the temperature employed, the diameter of the fibers, the particular pitch from which the fibers are prepared, and the mesophase content of such pitch. Generally, however, thermosetting can be effected in relatively short periods of time, usually in from about 5 minutes to less than about 60 minutes.

The temperature employed to effect thermosetting of the fibers must, of course, not exceed the temperature at which the fibers will soften or distort. The maximum temperature which can be employed will thus depend upon the particular pitch from which the fibers were spun, and the mesophase content of such pitch. The higher the mesophase content of the fiber, the higher will be its softening temperature, and the higher the temperature which can be employed to effect thermosetting. At higher temperatures, of course, thermosetting can be effected in less time than is possible at lower temperatures. Fibers having a lower mesophase content, on the other hand, require relatively longer heat treatment at somewhat lower temperatures to render them infusible.

A minimum temperature of at least 250° C. is generally necessary to effectively thermoset the fibers. Temperatures in excess of 500° C. may cause melting and/or excessive burnoff of the fibers and should be avoided. Preferably, temperatures of from about 275° C. to about 400° C. are employed. At such temperatures, the required amount of thermosetting can usually be effected within from about 5 minutes to less than about 60 minutes.

After the fibers have been thermoset as required, they are heated under compressive pressure to a temperature sufficiently elevated to cause the mesophase pitch in the unoxidized interior portions of the fibers to undergo liquid flow and exude through surface pores or flaws in the fibers, e.g., at a temperature of from about 400° C. to about 700° C. During such heating, small droplets of pitch appear at intervals along the fiber lengths and come into contact with the surfaces of the adjacent fibers. The pressure applied to the web during such

heating serves to compact the fibers and utilizes this bleeding to bond the fibers together into a dense, cohesive, self-bonded mass. When the web is then further heated to a carbonizing temperature in an oxygen-free atmosphere so as to expel hydrogen and other volatiles, infusible carbon bonds are formed between the fibers.

The pressure required to effect satisfactory compression and bonding of the fibers will, of course, vary with the degree to which the fibers have been thermoset, with the more highly oxidized fiber webs requiring more pressure than the lesser oxidized fiber webs. Generally, pressures of at least 5000 kPa are necessary to compress and bond the fibers into a platelike product having a density suitable for use as a brush material, e.g., in excess of 0.7 Mg./m<sup>3</sup>. At times, pressures in excess of 10,000 kPa may be necessary to attain a satisfactory product. While the use of an extraneous binder is not necessary to produce the selfbonded plates of the present invention, a binder may be employed, if desired to increase the density of the plate. Such binder, e.g., a mesophase pitch such as that from which the fibers themselves are produced, may be admixed with the fibers before they are compressed.

Upon further heating to a carbonizing temperature, the compressed mass is eventually rendered totally infusible. Upon heating to a temperature of about 1000° C., a dense, rigid body having a carbon content greater than about 98 percent by weight is obtained. At temperatures in excess of about 1500° C., the body is substantially completely carbonized. Such heating should be conducted in an oxygen-free atmosphere, such as the inert atmospheres described above to prevent further oxidation of the fibers.

Usually, carbonization is effected at a temperature of from about 1500° C. to about 2500° C. so as to produce a substantially completely carbonized body having a density greater than 0.7 Mg./m<sup>3</sup>. Generally, residence times of from about 0.5 minute to about 180 minutes are employed. While more extended heating times can be employed with good results, such residence times are uneconomical and, as a practical matter, there is no advantage in employing such long periods. In order to ensure that the rate of weight loss of the fibers does not become so excessive as to disrupt the fiber structure, it is preferred to gradually heat the fibers to their final carbonization temperature.

After the web has been compressed and carbonized, it may be further heated in an oxygen-free atmosphere, such as the inert atmospheres described above, to a graphitizing temperature in a range of from above about 2500° C. to about 3300° C., preferably from about 2800° C. to about 3000° C. A residence time of about 1 minute is satisfactory, although both shorter and longer times may be employed, e.g., from about 10 seconds to about 30 minutes, or longer. Residence times longer than 30 minutes are uneconomical and unnecessary, but may be employed if desired.

The carbonized or graphitized body produced in this manner is then impregnated with a thermosetting resin and heated to a temperature sufficiently elevated to cause the impregnant to thermoset, i.e., cure. Impregnation can be effected by any suitable means of effectively introducing the impregnant into the pores of the body. For example, the resin to be employed may be dissolved or suspended in a suitable solvent or dispersing agent and introduced into the pores of the body using conventional vacuum-pressure cycles.

After the body has been impregnated to the desired degree, it is heated to a temperature sufficiently elevated to cause the thermosetting resin impregnant to cure, e.g., from about 100° C. to about 200° C. After curing, the impregnated body generally contains from about 10 parts by weight to about 30 parts by weight of thermoset resin per 100 parts by weight of the body, preferably from about 15 parts by weight to about 25 parts by weight of thermoset resin per 100 parts by weight of the body.

The thermosetting resins used to impregnate the carbonized or graphitized body include, among others, phenolic resins, epoxy resins, furfuryl resins, and the like. Phenolic resins of the novolac type are preferred. Such resins are produced by condensing phenols, such as phenol itself, or resorcinol, with aldehydes such as formaldehyde, furfuraldehyde, acetaldehyde, and the like. Preferably, a phenol-formaldehyde resin, is employed. Conventional hardening agents, such as paraformaldehyde or hexamethylenetetramine, which upon the application of heat generate formaldehyde which reacts with the novolac resin and causes it to crosslink, are employed in the curing of these resins. The hardener for the resin is employed in an amount sufficient to cure such resin to the thermoset state, i.e., in an amount which will provide sufficient formaldehyde to react with and crosslink the resin.

Any inert solvent capable of dispersing or dissolving the thermosetting resin employed and vaporizable at a temperature lower than that at which the resin will cure can be employed. Generally, the thermosetting resin is present in the solution or dispersion in an amount of from about 5 percent by weight to about 75 percent by weight, preferably from about 20 percent by weight to about 50 percent by weight. Suitable solvents include, among others, saturated aliphatic hydrocarbons such as hexane, heptane, pentane, isoctane, purified kerosene, and the like; saturated cycloaliphatic hydrocarbons such as cyclopentane, cyclohexane, methylcyclopentane, dimethylcyclopentane, and the like; aromatic hydrocarbons such as benzene, toluene, xylene, and the like; and ketones such as acetone, and the like.

The impregnated bodies produced in this manner may then be cut into a desired shape and employed as an electromotive brush.

The following example is set forth for purposes of illustration so that those skilled in the art may better understand the invention. It should be understood that it is exemplary only, and should not be construed as limiting the invention in any manner.

#### EXAMPLE 1

A commercial petroleum pitch was treated to produce a mesophase pitch having a mesophase content of about 60 percent by weight. The precursor pitch had a density of 1.23 Mg./m<sup>3</sup>, a softening temperature of 122° C. and contained 1 percent by weight pyridine insolubles (P.I. was determined by Soxhlet extraction in boiling pyridine). Chemical analysis showed a carbon content of 94.1%, a hydrogen content of 5.56%, a sulfur content of 1.82% and 0.19% ash.

The mesophase pitch was produced by heating the precursor petroleum pitch at a temperature of about 400° C. for 18.5 hours under a nitrogen atmosphere.

After heating, the pitch contained 60.1 percent by weight pyridine insolubles, indicating that the pitch had a mesophase content of close to 60 percent. This pitch was then blow-spun through atomizing nozzles at a

11

temperature of 370° C. to produce staple lengths of fiber approximately 1-3 inches in length and 8 micrometers in diameter. The blow-spun fibers were deposited in intimately contacting relationship with each other on a wire mesh conveyor belt positioned beside the nozzle block by reducing the pressure behind the conveyor belt so as to draw the blow-spun fibers onto the belt. The fibers were allowed to collect on the belt until a fibrous web having an areal density of about 0.25 kg./m.<sup>2</sup> accumulated.

The fibrous web produced in this manner was then transported on the conveyor belt through a 12-meter long forced-air convection oven at a speed of 0.6 meter/minute. The oven contained eight zones, each 1.5 meters in length, and the web was gradually heated from 175° C. in the first or entrance zone to 400° C. in the eighth or exit zone while air was passed downward through the web and conveyor belt at a velocity of about 2 meters/minute. The oxygen content of the fibers was increased to 10 weight percent as a result of this procedure.

The thermoset fibrous web was then cut into circular discs 5 inches in diameter and approximately 200 grams of the discs were stacked in parallel fashion in a cylindrical graphite mold having an inner diameter of 5 inches and an inner depth of 12 inches. A graphite plate was placed on the stacked discs. The cylinder was placed in a small ceramic silo, surrounded with coke particles, and heated. When the temperature reached 250° C., a pressure of 6895 kPa was applied (in a direction parallel to the length of the cylinder) and maintained while the temperature was raised to 500° C. at a rate of 100° C. per hour. After heating for 15 minutes at 500° C., the pressure was released and the mold allowed to cool. A nitrogen atmosphere was maintained inside the silo throughout the heating and cooling periods.

A completely self-bonded plate was obtained in this manner which could be freely handled without loss of fibers. The plate was 1.791 cms. thick, and had a bulk density of 0.864 Mg./m.<sup>3</sup>

The plate produced in this manner was then heated to a temperature of about 1000° C. over a period of about 20 hours, and then to 3000° C. over a period of about 1 hour, and maintained at that temperature for 2 hours. After graphitization, the plate had a bulk density of 0.897 Mg./m.<sup>3</sup>, an elastic modulus of 1.66 GPa, a with-grain electrical resistivity of  $10 \times 10^{-4}$  ohm-centimeters, an against-grain electrical resistivity of  $495 \times 10^{-4}$  ohm-centimeters, and a resistivity ratio of 49.5:1.

The graphitized plate was cut into brushes approximately 2.5 cm.  $\times$  6.25 cm.  $\times$  1.25 cm. The brushes were placed in a vacuum chamber which was then evacuated to a pressure of 29 inches of mercury vac-

12

uum. A solution containing 1 part by weight of a phenolic resin (Bakelite BRP-5012, manufactured by Union Carbide Corporation) dissolved in 2 parts by weight of acetone was then introduced into the chamber to a level about 2.5 cms. above the graphite pieces. After thirty (30) minutes had elapsed, a pressure of 80-90 psi. was applied and held for 1 hour.

The impregnated pieces were then heated to 50° C. over a 30 minute period, then from 50° C. to 75° C. in 15 minutes where the temperature was maintained for 30 minutes, and then from 75° C. to 150° C. in 1 hour and held at 150° C. for 3 hours. The resin impregnant was fully thermoset by this treatment.

The impregnated brushes produced in this manner were then tested on a dummy commutator (copper) where brush life, contact drop and friction can be measured for a specific current density, commutator temperature, rubbing speed, and spring pressure but in which no current switching occurs. After 67.5 hours at 75 psi. current density, 8 lbs./sq. in. spring pressure, 8000 ft./min. rubbin speed, and 73° C. commutator temperature, the brushes showed a voltage drop of 3.14 volts and were determined to have a brush life of 5300 hours/inch and a coefficient of friction of 0.07. Conventional lampblack base electrographitic brushes in the same test showed a voltage drop of 2.56 volts and were determined to have a brush life of 1550 hours/inch and a coefficient of friction of 0.05.

When tested on a black band generator where commutating latitude could be measured by means of a "black" or sparkless commutation by adjusting the interpole current, at various current loads, until sparking occurred, the brushes prepared in accordance with the invention exhibited an average band (amperes) of sparkless commutation of 30.5 amperes as compared to an average band of 22.7 amperes for the conventional lampblack base electrographitic brushes. This test is described by J. C. Aydelott in "Black Band Method of Commutation Observations," Electrical Engineering, Vol. 60, pp. 446-451, June, 1941.

What is claimed is:

1. In an electromotive brush, the improvement wherein the brush is composed of a dense, rigid plate of self-bonded, non-woven carbon fibers formed from mesophase pitch fibers, said plate having a density in excess of 0.7 Mg./m.<sup>3</sup> and being impregnated with a thermoset resin.

2. An electromotive brush as in claim 1 wherein the fibers are graphite fibers.

3. An electromotive brush as in claim 1 wherein the fibers are non-graphitic carbon fibers.

\* \* \* \*

55

60

65

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 4,140,832

Dated February 20, 1979

Inventor(s) Daniel J. Menegay

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Summary sheet, "Schultz" should read -- Schulz -- (two occurrences).

Column 2, line 28, after "temperature" insert -- above --.

Column 4, line 29, "an" should read -- in --.

Column 5, line 10, "flouranthene" should read -- fluoranthene --.

Column 7, line 36, "provides" should read -- provided --.

Column 9, line 18, "selfbonded" should read--self-bonded --.

Column 9, line 19, insert a comma (,) after "desired".

Column 9, line 32, insert a comma (,) after "above".

Column 10, line 26, "reach" should read -- react --.

Column 12, line 21, "rubbini" should read -- rubbing --.

Signed and Sealed this

Twenty-sixth Day of June 1979

[SEAL]

Attest:

RUTH C. MASON  
*Attesting Officer*

DONALD W. BANNER  
*Commissioner of Patents and Trademarks*

# United States Patent [19]

Selover, Jr. et al.

[11] 4,014,730

[45] Mar. 29, 1977

[54] POLYMER DENSIFIED GRAPHITE SHEET AS IMPERVIOUS CONNECTOR FOR AN ELECTRICAL CAPACITOR

[75] Inventors: Theodore B. Selover, Jr., Shaker Heights; Donald L. Boos, Garfield Heights; Thomas H. Hacha, Willoughby, all of Ohio

[73] Assignee: Standard Oil Company, Cleveland, Ohio

[22] Filed: July 31, 1974

[21] Appl. No.: 493,278

## Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 385,435, Aug. 3, 1973, which is a continuation-in-part of Ser. No. 251,225, May 8, 1972, abandoned.

[52] U.S. Cl. .... 156/331; 156/60; 156/327; 156/333

[51] Int. Cl.<sup>2</sup> .... B05D 7/24

[58] Field of Search .... 427/81, 113, 115, 294, 427/370, 385, 80; 156/60, 327, 333, 331

## [56] References Cited

### UNITED STATES PATENTS

2,820,728	1/1958	Burns, Jr. ....	427/113
2,962,386	11/1960	Doll et al. ....	427/294
3,120,454	2/1964	Bailey et al. ....	427/113
3,648,126	3/1972	Boos et al. ....	317/230
3,656,027	4/1972	Isley ....	317/230

### FOREIGN PATENTS OR APPLICATIONS

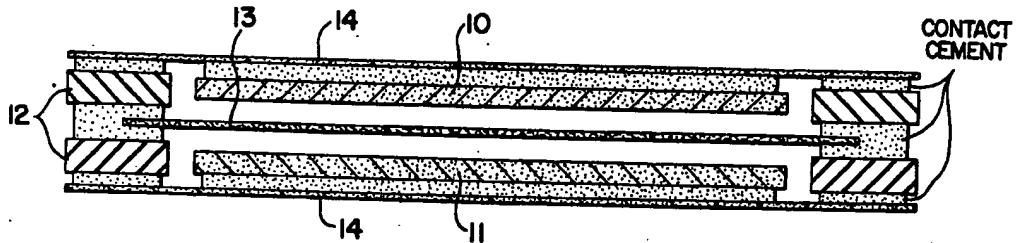
1,090,566	3/1960	Germany ....	427/113
-----------	--------	--------------	---------

Primary Examiner—Cameron K. Weiffenbach  
Attorney, Agent, or Firm—Herbert D. Knudsen; Evelyn R. Kosman; John F. Jones

## [57] ABSTRACT

The connector of this invention comprises a thin, flexible sheet of graphite in which the pores and voids of the graphite are filled with a polymer to render the graphite impervious to the electrolyte of the capacitor.

5 Claims, 2 Drawing Figures



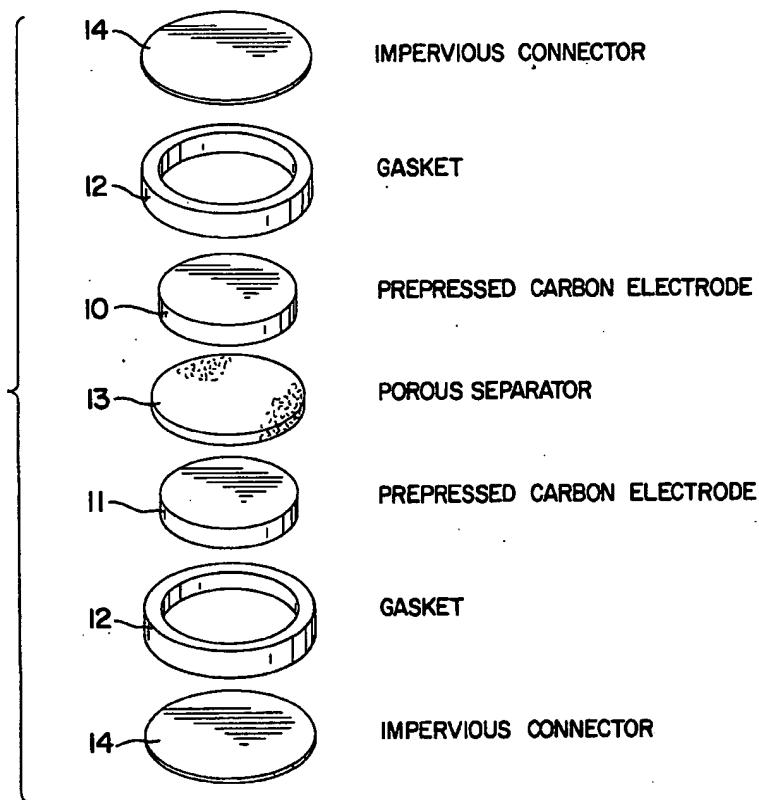


FIG. 1

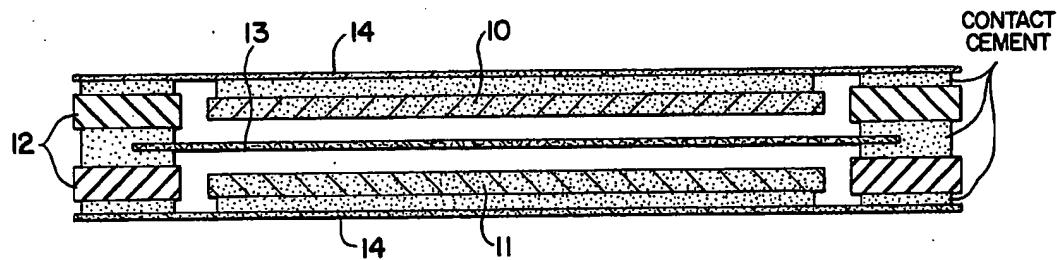


FIG. 2

**POLYMER DENSIFIED GRAPHITE SHEET AS  
IMPERVIOUS CONNECTOR FOR AN  
ELECTRICAL CAPACITOR**

This is a continuation-in-part application of our co-pending patent application Ser. No. 385,435 filed Aug. 3, 1973 which in turn is a continuation-in-part of patent application Ser. No. 251,125 filed May 8, 1972, now abandoned.

This invention relates to an improved electrically-conductive, impervious connector for use in an electrical capacitor. More particularly, this invention relates to an intercell electron-conducting, ion-insulation connector that is chemically inert to the corrosive electrolyte of a capacitor operated at elevated temperatures, and is particularly useful in a capacitor having paste electrodes as described in U.S. Pat. Nos. 3,536,963, 3,634,736 and 3,656,027.

The connector which is the subject of the present invention comprises a thin, porous, flexible sheet of graphite which has been densified with a polymer. The term "densify" as employed in this invention refers to filling some of the pores and voids of the graphite sheet with a polymeric filler. This connector represents an improvement over that described in U.S. Pat. No. 3,656,027 which discloses an electron-conducting connector comprising a single metal or graphite substrate having an electrically-conductive, carbon filled polymer laminated to one side of the substrate. It is surprising in view of the prior art that the connector of the present invention composed of graphite sheet which has been impregnated with a non-conductive polymer would be sufficiently conducting to be suitable for the purpose intended here, and it is more surprising that a capacitor containing this connector actually displays a lower equivalent series resistance than one containing a connector of the prior art.

One of the main advantages associated with the connector of the present invention is its ease of manufacture and reproducibility. By eliminating a number of processing steps, it is more simple and less costly to fabricate. Further, it overcomes the problems associated with increased resistance due to poor bonding between the substrate and the polymer, and it contributes less resistance to the equivalent series resistance of the capacitor due to the direct contact between the carbon electrode and the highly conductive graphite sheet.

The connector of this invention is characterized as having chemical and thermal stability in the presence of a strong oxidizing acid at elevated temperatures, it meets the requirements for use in a capacitor that operates within the temperature range of about -40° to about 100° C., and it also sustains low liquid and gas permeability under the aforementioned conditions throughout the life of the capacitor.

The graphite sheet or foil comprising the connector of this invention may consist of any available thin, flexible, graphite sheet or foil having a thickness in the range of generally from about 0.3 to 10 mils. Sheet or foil having a thickness above this range generally contributes excessively to the resistance of the capacitor while thinner sheet or foil is usually too fragile for practical purposes.

Readily available forms of graphite sheet that are suitable for this purpose are graphite sheet prepared from expanded, compressed, graphite particles, and having anisotropic electrical properties, as described in

U.S. Pat. No. 3,404,061, and wherein the anisotropy ratio, i.e., the ratio of the specific conductivity along the surface plane "A" to the specific conductivity along the perpendicular plane C is between 1 and 1000

5 at room temperature. The graphite sheet need not be limited to these types of graphite, however, and any electrically-conductive, flexible graphite sheet or foil falling within the desired range of thickness is operable.

The available flexible graphite sheet or foil possesses 10 all of the desired properties for use as a chemically stable electrical connector with the exception of porosity. Untreated graphite sheet or foil is too porous for the purpose intended in this invention, and it acts as a wick which readily absorbs the electrolyte from the 15 capacitor. In accordance with this invention, in order to render the graphite sheet impermeable, the graphite sheet is impregnated with a polymeric filler or sealant.

The polymers suitable as sealants for the connector of this invention are the natural rubbers and the synthetic rubbers obtained from ethylene, propylene, isobutylene, butadiene, isoprene, chloroprene, copolymers of styrene-butadiene, copolymers of isobutylene with various conjugated dienes wherein the amount of the diene does not exceed about 5 mole percent, as for example the butyl rubbers, chlorobutyl rubbers, chlorosulfonated polyethylene, vinylidene fluoride polymers, polybutadiene-urethane polymers, polyarylsulfones, ethylene-propylene terpolymers, nitrile rubbers, and Thiokol rubbers. Preferred are the butyl rubbers, 30 and copolymers of vinylidene fluoride-hexafluoro-propylene and butadiene-urethane because of their chemical stability and their low permability.

It is essential that the polymeric sealant of this invention be in a fluid form so it can readily penetrate the pores and voids of the graphite. Particularly applicable are the low molecular weight, low viscosity, semi-liquid pre-polymers capable of curing in situ, such as the low molecular weight butyl rubbers. Also suitable are solvent solutions of the higher molecular weight elastomers. Suitable solvents include aliphatic, aromatic and naphthenic hydrocarbons, ketones and esters, and solvents such as for example, toluene, xylenes, cyclohexane, n-hexane, acetone, methyl ethyl ketone, ethyl acetate and amyl acetate are especially preferred. Solutions containing from about 10 to about 40 percent by weight of the elastomer in the appropriate solvent have been found to be satisfactory for incorporation into the graphite.

The polymeric sealants may be incorporated into the 50 pores of the graphite sheet by any one of several methods known to those skilled in the art. For example, solvent solutions of an elastomer may be applied by vacuum impregnating, while more viscous polymers such as low molecular weight elastomers may be more readily applied to the surface of the graphite by spray coating, brush coating, and the like, covered with a second sheet of graphite, and the elastomer forced into the pores of the graphite and the excess exuded from between the two sheets of graphite by means of pressure, so that the ultimate composite comprises solely a laminate of two layers of elastomer-filled graphite sheet.

Where the sealant is an elastomer, it is advantageous to seal the elastomer in the pores of the graphite by curing in order to further improve impermeability and chemical stability. Curing of the elastomer-impregnated graphite may be accomplished by exposure to nuclear radiation, ultraviolet light, infrared radiation,

steam, hot air, and preferably, vulcanization under pressure. In the vulcanizing treatment, the elastomer is mixed with the usual vulcanizing agents such as accelerators, antioxidants, antiozonants, waxes, stabilizers, and the like, before it is applied to the graphite sheet, and the entire graphite-rubber composite is subjected to a cure at elevated temperatures and pressures.

The pressure, temperature, and time suitable for vulcanizing the elastomer-filled graphite may vary with the cure time and flow characteristics of the particular elastomer used. It is also advantageous to preheat the elastomer-filled graphite without the application of any pressure to allow for gases, such as, water vapor and solvent to escape before vulcanizing.

Generally, the rubber-filled graphite may be cured at temperatures ranging from about room temperature to about 220° C and at pressures of from about 15 to about 15,000 psi, for a period of time ranging from about 1 minute to about 24 hours, depending on the temperature of cure and type of polymer employed. For example, an elastomer may be cured at room temperature for a period of 24 hours. Preferably, curing is carried out by preheating the rubber-graphite composite to a temperature in the range of about 90° to 120° C, for a period of about 1 to 2 minutes and curing at a temperature in the range of 105° to 175° C, at a pressure of about 250 to 13,500 p.s.i. for one minute to 16 hours.

The invention will be more readily understood from the following detailed description taken in conjunction with the drawings wherein an exploded view of the components parts of a single cell electrical capacitor containing the impervious connector is shown in FIG. 1, and a cross sectional view of the assembled cell is shown in FIG. 2.

The cell shown is an example of a paste electrode capacitor which essentially comprises a pair of carbon paste electrodes 10, 11, a porous separator 13, and a pair of electron-conducting and ionic-insulating connectors 14. The primary functions of connector 14 are as a current collector and an inter-cell ionic insulator. While FIG. 2 illustrates one embodiment of the capacitor of this invention, in another preferred embodiment, however, the inner surfaces of connectors 14 are in direct contact with the outer surfaces of electrodes 10 and 11.

An annular means or a gasket 12 is preferably cemented or in some manner affixed to conducting member 14. Since paste electrodes 10 and 11 are not rigid masses but are to some extent flexible, the principle function of gasket 12 is to confirm the electrodes 10 and 11 and prevent the mass of the electrode method from seeping out. The gasket is constructed from an insulating material and is flexible to accommodate expansion and contraction of the electrode and flexing of the cell.

Separator 13 is generally made of a highly porous material which functions as an electronic insulator between the electrodes yet allows free and unobstructed movement to the ions in the electrolyte. The pores of the separator 13 must be enough to prevent contact between the opposing electrodes, since such a condition would result in a short circuit and consequent rapid depletion of the charges accumulated on the electrodes. Generally, conventional battery separators may be utilized, however, the separator can also be a non-porous ion-conducting films, such as an ion-exchange membrane. Prior to its use it is advantageous to

saturate the separator with electrolyte. This can be accomplished by soaking the separator in the electrolyte for a period of time of up to about 15 minutes.

The carbon electrodes 10 and 11 consist of activated carbon particles in admixture with the electrolyte. Because electrical energy storage of a capacitor is apparently based on surface area, an increase in energy storage can be expected from an increase in surface area of carbon particles, as by activation. A detailed description of the electrical capacitor having carbon paste electrodes is more fully disclosed in U.S. Pat. No. 3,536,963.

Paste electrode 11 may also comprise a paste formed from the electrolyte in admixture with solid particles of boron carbide or a refractory hard metal carbide or boride wherein the metal may comprise tantalum, niobium, zirconium, tungsten and titanium, as more fully disclosed in U.S. Pat. No. 3,634,736. Also, paste electrode 11 may comprise a mixture of the electrolyte and a metal powder of copper, nickel, cadmium, zinc, iron, manganese, lead, magnesium, titanium, silver, cobalt, indium, selenium and tellurium, as disclosed in U.S. Pat. No. 3,648,126.

The electrolyte may consist of a highly conductive medium such as an aqueous solution of an acid, base or salt. In applications wherein high conductivity is required, 30 percent sulfuric acid is especially preferred. Non-aqueous electrolytes can also be used, and solutes such as metal salts of organic and inorganic acids, ammonium and quaternary ammonium salts, and the like may be incorporated in organic solvents.

In instances where one electrode may comprise a metal powder in admixture with the electrolyte, it is essential that the electrolyte be a non-corrosive media, such as a base, salt or non-aqueous media. In the assembly of the cell, the component parts are assembled in the order as shown in the accompanying FIGS. 1 and 2, and the cell is then compressed at a pressure sufficient to render the unit a coherent structure. Pressures in the range of about 240 psi have been found sufficient for this purpose.

#### EXAMPLE 1

The graphite connector utilized in this example was prepared as follows:

A. The butyl rubber filler was prepared by combining the following components in the amounts indicated:

	Parts by weight
Isobutylene-isoprene copolymer (Enjay, 4.2 mol% unsaturation, visc. aver. mol wt. 32,500)	100
White oil (Visc. at 100° F-51SSU, $d_{40}^{\circ}$ F 0.82g/cc, free of unsaturation and aromatics)	75
zinc oxide	5
Stearic acid	1
4A Molecular Sieves	5
Paraoquinone dioxide	3.5
$Pb_2O_4$	8.0
2,2'-benzothiazyl disulfide	5.0

The above components were mixed in a kneader with the resulting uniform blend being pourable at room temperature;

B. The liquid mixture was heated with stirring to 65° C and spread on the surface of a sheet of graphite, 5 mils thick, prepared from expanded, compressed

graphite particles, as described in U.S. Pat. No. 3,404,061.

C. A second sheet of graphite was placed over the elastomer-coated graphite sheet obtained in (B) and the two sheets of graphite were compressed under light pressure to impregnate the graphite with rubber and to remove excess rubber from between the two graphite sheets. The composite thus formed was then cured between two sheets of degreased aluminum foil for 10 minutes at 165°C and at a pressure of 13,000 psi.

D. A cell was constructed as shown in FIG. 1, utilizing the above-prepared connector. The capacitor contained a pair of carbon paste electrodes, 1.125 inch in diameter, prepared from activated carbon (Nu-Char Activated Carbon C-115, West Virginia Pulp and Paper Company), having a surface area of 700-950m<sup>2</sup>/g; an electrolyte consisting of 30 percent aqueous sulfuric acid; an ionically conducting separator, 1.125 inch in diameter and 3 mils thick, prepared from an anisotropic membrane, the membrane having a resistivity in 40 percent KOH of 3.8 ohm-cm; and a pair of gaskets constructed from a copolymer of vinylidene fluoride and hexafluoropropylene, (Viton) having a thickness of 0.015 inch, an I.D. of ½ inch and an O.D. of 1.125 inch. The assembled cell was placed in a clamp and a 1.25 inch (I.D.) retaining ring slipped over the capacitor and cylinder assembly. The cell was compressed under a pressure of 240 psi.

The equivalent series resistance of the cell was measured at room temperature and was found to be 17 milliohms, and the leakage current of the cell measured 1.6 milliamperes. At 85°C the equivalent series resistance of the cell measured 14 milliohms and the leakage current 2.7 milliamperes.

#### EXAMPLE 2

A rubber-impregnated graphite connector was prepared according to the following procedure:

A. The rubber was prepared by mixing the following components in the amounts indicated, in a Banbury mixer at 71°C for 15 minutes:

	Parts by weight
Isobutylene-isoprene copolymer (Enjay, 2.1 - 2.5 mol% unsaturation, visc. aver. molecular wt. - 3.5 × 10 <sup>5</sup> )	100
Zinc oxide	5
Stearic acid	2
Paraffin wax	2
(B) The following components were added to the mixture obtained from step (A) during milling:	
2-Mercaptobenzothiazole	0.75
Tetramethylthiuram disulfide	1.25
Sulfur	2

The mixture was added to the banded rubber and thoroughly mixed and sheeted out through water cooled mill rolls;

C. The sheeted, uncured rubber obtained in step (B) was dissolved in toluene to a concentration of 7% by weight of rubber solids;

D. Flexible graphite foil, 5 mils thick using the same graphite sheet as employed in Example 1, was vacuum-impregnated with the toluene solution obtained from (C) and the excess liquid was removed from the surface of the graphite;

- E. The impregnated graphite sheet was pressure-cured at a temperature of 165°C and a pressure of 4000 psi, for 30 minutes between degreased aluminum foil contact surfaces on open air platens;
- F. A cell was constructed and assembled, as in Example 1, utilizing the above-prepared connectors. The equivalent series resistance and the leakage current of the cell measured at room temperature were in the same range as those of Example 1.

#### EXAMPLE 3

The electrical resistance of samples of butyl rubber (Butyl-365, Enjay Chemical Co.) containing various levels of extra conductive furnace black (Vulcan XC-72 Cabot Corp.) ranging from 0 to 100 parts of furnace black per hundred parts of rubber, by weight, were measured at room temperature. In addition to the carbon black, the rubber samples contained the following components in parts per 100 parts of rubber:

Component	Parts by weight per 100 parts of rubber
Stearic acid	2
Zinc oxide	5
Paraffin	2
Sulfur	2
Mercaptobenzothiazole	0.75
Tetramethylthiuram disulfide	1.25

After mixing, the above samples were sheeted out to a thickness of 10 mils on a differential roll mill. They were then vulcanized between two sheets of chrome-plated metal in a hydraulic press that was maintained at a temperature of 160°C, and a total force of 25,000 pounds for 20 minutes. The electrical resistance of these rubbers are shown in the following table.

Table I

	Parts carbon black in 100 parts butyl rubber, by weight	Electrical Resistance ohms in. <sup>2</sup> /mil
20	212,000	
30	36,500	
40	417	
50	8.5	
75	0.0047	
100	0.002	

These data indicate that the butyl rubber samples containing less than about 50 parts of carbon black per hundred parts of rubber are insulators, and therefore these data substantiate the unobviousness of the present invention. For it is unexpected that a connector, as one described in this invention utilizing non-conductive rubber as a filler for graphite, would exhibit the high conductivity shown in the examples.

We claim:

1. A process for preparing an electron-conducting, ion-insulating connector for use in an electrical capacitor comprising the following steps in sequence:
  - a. coating a single surface of a thin, flexible, porous, sheet of graphite having a thickness within the range of about 0.3 to 10 mils with a viscous paste of an elastomer containing a vulcanizing agent, said elastomer being a member selected from the group consisting of butyl rubber, copolymers of butadiene-urethane and vinylidene fluoride-hexafluoropropylene;

- 7  
b. covering the elastomer-coated surface on the graphite with a second sheet of the graphite, forming a composite;  
c. compressing the composite formed in (b) under sufficient pressure to impregnate the two sheets of graphite with elastomer and to exude any excess elastomer from therebetween so as to form a laminate of essentially the two sheets of elastomer-impregnated graphite; and  
d. vulcanizing the elastomer-impregnated laminate obtained in (c) at a temperature of from about 25° to 220° C and a pressure of from about 15 to 15,000 psi.

2. The process of claim 1 wherein the thickness of the graphite sheet is within the range from about 0.3 mils to 10 mils.  
3. The process of claim 1 wherein the elastomer is butyl rubber.  
4. The process of claim 3 wherein the graphite sheet is composed of expanded, compressed graphite particles having anisotropic electrical properties.  
5. The process of claim 4 wherein the elastomer-impregnated graphite sheet is cured by vulcanizing at a temperature within the range of 105° to 175° C and at a pressure of from 250 to 13,500 psi.  
\* \* \* \* \*

15

20

25

30

35

40

45

50

55

60

65

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 4,014,730 Dated March 29, 1977

Inventor(s) Theodore B. Selover, Jr. et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1: Line 9, "251,125" should be -- 251,225 --

Column 1: Line 40, "maufacture" should be -- manufacture --

Column 2: Line 32, "permability" should be -- permeability --

Column 3: Line 61, after "must be" insert -- small --

Column 6: Line 37, "These" should be -- these --

Column 7: Line 12, after "and" delete "a"

Column 7: Line 12, "pessure" should be -- pressure --

Column 8: Line 10, "curved" should be -- cured --

Signed and Sealed this

*Thirty-first Day of January 1978*

[SEAL]

Attest:

RUTH C. MASON  
*Attesting Officer*

LUTRELLE F. PARKER  
*Acting Commissioner of Patents and Trademarks*

United States Patent [19]  
Greinke et al.

US005228701A

[11] Patent Number: 5,228,701  
[45] Date of Patent: Jul. 20, 1993

[54] FLEXIBLE GRAPHITE ARTICLES WITH AN AMORPHOUS CARBON PHASE AT THE SURFACE

[75] Inventors: Ronald A. Greinke, Medina; Ronald A. Howard, Brook Park, both of Ohio

[73] Assignee: UCAR Carbon Technology Corporation, Danbury, Conn.

[21] Appl. No.: 590,582

[22] Filed: Sep. 28, 1990

Related U.S. Application Data

[63] Continuation of Ser. No. 171,663, Mar. 22, 1988, abandoned.

[51] Int. Cl.<sup>5</sup> ..... F16J 15/30

[52] U.S. Cl. ..... 277/102; 277/112; 277/123; 277/125; 277/227; 277/237 R; 277/DIG. 6; 264/291; 264/335; 427/227; 427/228; 428/244; 428/408

[58] Field of Search ..... 277/102, 112, 123, 125, 277/227, 237 R, DIG. 6; 427/227, 228, 428/408, 244; 264/291, 335

[56] References Cited

U.S. PATENT DOCUMENTS

- |           |         |               |           |
|-----------|---------|---------------|-----------|
| 3,404,061 | 10/1968 | Shane et al.  | 428/408 X |
| 3,661,401 | 5/1972  | Farnam        | 277/227   |
| 3,914,508 | 10/1975 | Hooton et al. | 428/408   |

4,068,853	1/1978	Schnitzler	277/204 X
4,082,300	4/1978	Harbeck et al.	277/123
4,169,185	9/1979	Bhatia	277/235 B X
4,178,413	12/1979	De Munda	428/408
4,190,257	2/1980	Schnitzler	277/102
4,279,952	7/1981	Kodama et al.	428/408 X
4,321,298	3/1982	Shaffer et al.	428/408 X
4,391,873	7/1983	Brassell et al.	428/408 X
4,456,645	6/1984	Chi	428/408 X
4,483,539	11/1984	Bindel et al.	277/235 B X
4,490,828	12/1984	Fukuhara et al.	219/553 X
4,526,911	7/1985	Boxall et al.	523/445
4,643,956	2/1987	Sandelli et al.	429/34
4,759,977	7/1988	Fukuda et al.	428/408 X
4,826,181	5/1989	Howard	277/112

FOREIGN PATENT DOCUMENTS

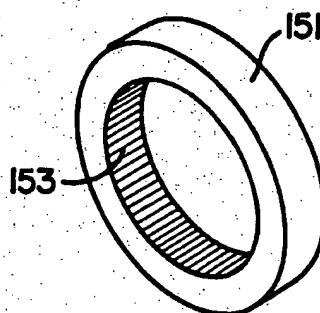
2053829	4/1971	France	277/235 B
52-11354	1/1977	Japan	277/235 B
551311	5/1977	U.S.S.R.	428/408
1018438	1/1966	United Kingdom	427/227

Primary Examiner—William A. Cuchlinski, Jr.  
Attorney, Agent, or Firm—F. J. McCarthy

[57] ABSTRACT

An article, such as a seal ring, suitable for reduction of chatter when used in stuffing boxes with reciprocating stems. The article has an amorphous carbon phase at the surface of the article with the amorphous carbon phase extending into the article from the surface.

25 Claims, 2 Drawing Sheets



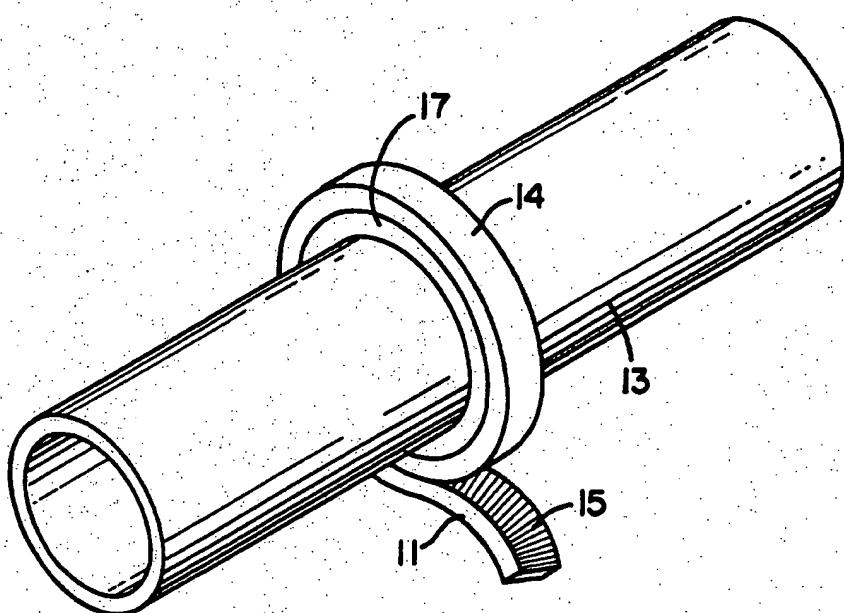


FIG. 1a

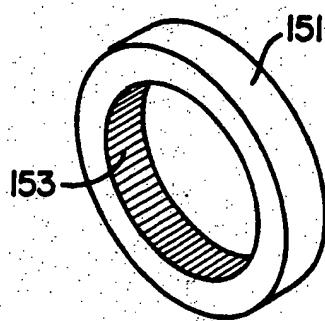


FIG. 1b

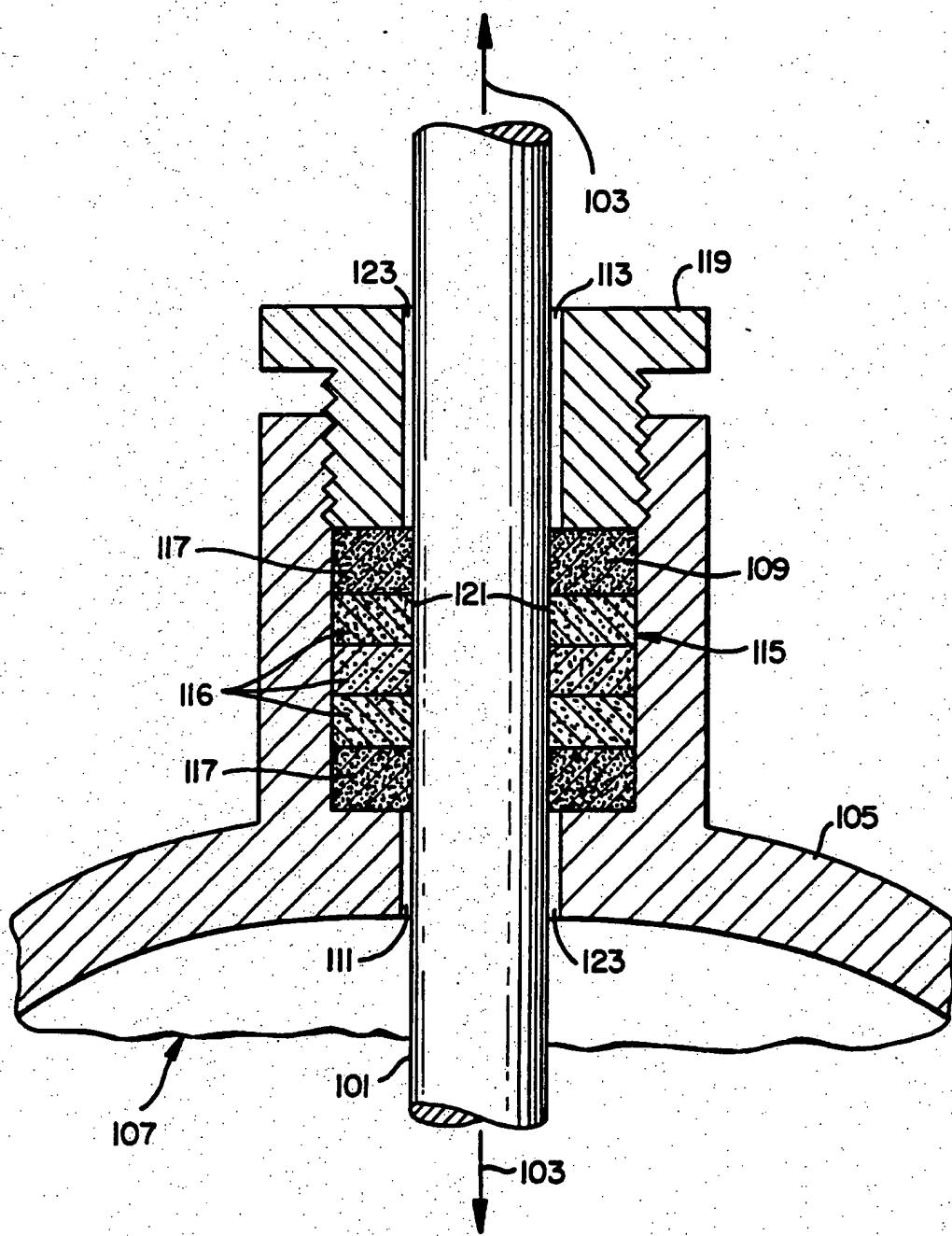


FIG. 2

## FLEXIBLE GRAPHITE ARTICLES WITH AN AMORPHOUS CARBON PHASE AT THE SURFACE

This application is a continuation of prior U.S. application Ser. No. 171,663 filed Mar. 22, 1988, now abandoned.

### FIELD OF THE INVENTION

The present invention relates to flexible carbon seal rings for seals around reciprocating valve stems and pump shafts.

### BACKGROUND OF THE INVENTION

Flexible graphite has been successfully used as a packing material in fluid handling devices, such as pumps and valves, to provide a seal where a reciprocating stem or shaft enters the device. Commonly the flexible graphite is in the form of preformed annular rings which are placed around the stem in a stuffing box and compressed. For example, U.S. Pat. No. 4,190,257 discloses packing rings of flexible graphite particles compressed together into annular seal rings. Packing seal rings of flexible graphite may also be formed by wrapping a flexible graphite tape about a shaft to form an annular shaped article and compressing the article in a die.

Flexible graphite seal rings, since they are essentially pure carbon, are chemically inert and stable at high temperatures. In addition, the resilience of the flexible graphite allows for very effective seals. Because of these qualities, flexible graphite is a preferred packing material in high temperature and corrosive environments.

However, packings with flexible graphite seal rings are prone to produce "chatter" when used as seals for reciprocating valve stems. Particularly at temperatures less than about 1100° F. (600° C.). Chatter is an erratic slip-stick motion of the stem as it passes through the packing. It is a common phenomenon. Particularly in applications where little force is being applied to the stem to move it through the packing or where precise control is required. Such applications include pneumatically controlled valves wherein a diaphragm or piston actuates a reciprocating stem. Because of chatter, precise control of such valves is difficult or impossible.

Chatter can be reduced by applying a lubricious material on the surface of the stem, such as water, Petroleum derivatives, or the like. However, these materials generally provide only a temporary solution as they often volatilize or degrade, particularly when the valve is subject to high temperatures. The loss of the lubricious material then results in the return of the chatter of the stem.

### OBJECTS OF THE INVENTION

An object of the invention is to provide flexible graphite seal rings that effectively reduce chatter when used in conventional stuffing boxes.

Another object of the invention is to provide seal rings with a permanent surface that reduces chatter when used in a conventional stuffing box and does not degrade or volatilize at high temperatures.

Another object of the invention is to provide flexible graphite seal rings that will reduce chatter in a conventional stuffing box wherein the chemical inertness and

high temperature stability of the seal rings is not compromised.

### SUMMARY OF THE INVENTION

5 An embodiment of the invention is an article comprising flexible graphite with a continuous amorphous carbon phase on a surface of the article, the amorphous carbon phase extending from said surface into the interior of the article. The amorphous carbon surface, i.e. 10 the surface with the amorphous carbon phase, is typically adapted to bear against a moving stem to provide a chatter-free seal. In a preferred embodiment, a lubricious material is applied over the amorphous carbon surface.

15 Another embodiment of the invention is a method for manufacturing a flexible graphite article with an amorphous carbon surface comprising:

(a) compressing exfoliated graphite flakes into an article having a density between 0.05 and 2.0 g/cm<sup>3</sup>, preferably g/cm<sup>3</sup> between 0.05 and 1.5 g/cm<sup>3</sup>, more preferably between 0.1 and 0.5 g/cm<sup>3</sup>;

(b) applying a coke forming organic material upon a surface of the article; and

(c) subjecting the article to a temperature sufficient to coke the organic material to form an amorphous carbon phase upon the surface of the article.

The amorphous carbon phase is continuous at the surface, i.e. there is an uninterrupted path through the amorphous carbon phase at the surface. However, the continuous amorphous carbon phase may contain small islets of one or more compressed flexible graphite flakes dispersed throughout the amorphous carbon at the surface. Thus, the surface may comprise a continuous amorphous carbon phase and flexible graphite, or comprise the continuous amorphous carbon phase with no flexible graphite present. For simplicity, reference to the "amorphous carbon surface" shall refer herein to any surface of an article of the invention which has an amorphous carbon phase at the surface, even though there may also be flexible graphite at the same surface.

The amorphous carbon phase extends from the surface into the interior of the flexible graphite article. The volume fraction of the amorphous carbon phase is greatest at the surface and diminishes as the amorphous carbon phase extends into the interior of the article, with no distinct phase boundary between the amorphous carbon phase and the flexible graphite. Typically the amorphous carbon phase extends into the flexible graphite article about 5 mils (0.13 mm), although this will vary, depending on the penetration of the coke forming organic material, which may be in turn affected by the wetting and viscosity properties of the coke forming organic material, the density of the flexible graphite, and other factors.

Because of the penetration of the amorphous carbon phase into the interior, wear or attrition of the amorphous carbon surface presents new amorphous carbon at the surface, so there continues to be an amorphous carbon phase on the surface. Accordingly, the articles of the invention provide an amorphous carbon surface that will not quickly wear off or degrade with use. For a seal ring for a reciprocating stem, the amorphous carbon phase on the surface does not flake off or significantly degrade with use, and provides chatter-free operation for periods much longer than was possible with prior seals. The amorphous carbon phase provides an essentially chatter-free, wear resistant bearing surface.

for the reciprocating stem, whereas the flexible graphite provides the resiliency to form a seal against passage of fluids.

The amorphous carbon phase is predominately non-crystalline carbon formed by carbonization or coking of the organic material. However, it is understood that the amorphous carbon phase may be partially crystalline, and contain ordered or partially graphitic molecular structures.

The articles of the invention with an amorphous carbon surface can be formed by first compressing exfoliated graphite flakes into a flexible graphite article, preferably a sheet, to a density between 0.05 and 2.0 g/cm<sup>3</sup>. The density should be sufficiently high to provide adequate strength of the article for handling, but is preferably as low as possible to assist penetration of the organic material when it is applied. The preferred densities are less than 1.5 g/cm<sup>3</sup>, more preferably between 0.1 and 0.5 g/cm<sup>3</sup>.

Exfoliated graphite flakes from which the flexible graphite article are formed are graphite flakes which have been treated with an intercalating agent, such as a mixture of sulfuric and nitric acid, and exposed to a high temperature, for example about 1000° C., to cause the flakes to expand in the c-direction. Flexible graphite is a material consisting essentially of graphite formed by compressing exfoliated graphite flakes into a coherent shape or article, preferably a sheet. Production of exfoliated graphite flakes and the production of flexible graphite therefrom is disclosed in U.S. Pat. No. 3,404,061, which is hereby incorporated by reference.

After formation of the flexible graphite article, a coke forming organic material is then applied to its surface. By "coke forming" is meant the ability to form amorphous carbon when the material is subjected to elevated temperatures. When the organic material is applied to the surface, the organic material should penetrate into the article from the surface. When the organic material is thereafter coked, an amorphous carbon phase is formed that extends from the surface into the interior of the object, and provides a surface with a continuous phase of amorphous carbon.

Penetration of the organic material into the surface of the flexible graphite article can be achieved by applying the organic material as a liquid with a sufficiently low viscosity. Alternately, the organic material may be applied as a solid or viscous liquid, and heated, or treated with a solvent, to soften or liquify the organic material and cause penetration of the organic material into the surface.

If the organic material is a thermosetting resin, the article may be subjected to conditions to cure the organic material. Curing may not be required if carbonization of the organic material results in a satisfactory amorphous carbon phase.

After application of the organic material, the article may be further compressed to a higher density to increase strength of the article and ease further handling of the article.

The treated article is then heated to a temperature sufficient to coke the organic material and form an amorphous carbon phase. For most applications, the organic material should be carbonized at a temperature higher than the temperature to which the article will be exposed during use. For most organic materials, carbonizing in a non-oxidizing atmosphere between 450° C. and 1000° C. is suitable.

In a preferred method of the invention, a lubricious material is applied upon the top of the amorphous carbon phase. The lubricious material may be any material with lubricious properties which is compatible with flexible graphite and amorphous carbon. While almost any liquid provides some lubricity, preferred materials are those which are stable under the environmental conditions to which the article may be subjected. In addition, the lubricity should preferably not degrade significantly during use. Suitable lubricious materials include liquid organic and inorganic lubricants.

Preferably the article of the invention is an annular seal ring of flexible graphite, with the amorphous carbon surface corresponding to the inner cylindrical surface of the seal ring which faces inwardly, and which is the surface adapted to bear against a stem to provide a seal against fluid leakage. A seal ring may be produced by any suitable method, such as wrapping flexible graphite sheet around a shaft with the amorphous carbon surface towards the shaft and axially compressing the resulting annular shaped article.

By use of seal rings of the invention, chatter can be significantly reduced or eliminated. A seal ring of the invention with an amorphous carbon surface which has been treated with a lubricious material is the most effective in reducing chatter and typically does not require a break-in period. Usually amorphous carbon surfaces which have not been treated with a lubricious material significantly reduce chatter, with chatter being completely eliminated after a break-in period.

The amorphous carbon surface of the seal ring of the invention, is carbon as is the flexible graphite, and therefore, retains its anti-chatter properties at high temperatures. Accordingly, the seal rings of the invention may be used for fire safe valves, that is valves that will function after being subjected to high temperatures. The optional lubricious materials applied to the amorphous carbon surface are generally lost at elevated temperatures, so there may be a slight loss in the anti-chatter property at high temperatures for amorphous carbon surfaces treated with a lubricious material. In general the lubricious material contributes to eliminating chatter up to the point the lubricious material breaks down or volatilizes, about 225° C. for ferric stearate, and about 250° C. for polytetrafluoroethylene. The amorphous carbon surface provides chatter reduction after being exposed to temperatures as high as 450° C. in air, and 3000° C. in non-oxidizing environments.

It is preferable to treat the amorphous carbon surface with a lubricious material, even if the article may be subjected to temperatures sufficient to remove the lubricious material. It has been found that treatment of the amorphous carbon surface with a lubricious material significantly reduces the break-in time of the surface. For a new seal ring of the invention with an untreated amorphous carbon surface, there is a slight chatter which continues over several hundred cycles before disappearing. In contrast, if the amorphous carbon surface of a new seal ring is treated with a lubricious material, chatter is usually eliminated beginning with the first cycle. After a break-in of about a hundred cycles, the seal ring will usually remain chatter free, even if the lubricious material is volatilized, leaving only the amorphous carbon surface.

The articles of the invention having an amorphous carbon surface may be used where chatter or a related phenomenon is a problem. Possible applications are as seal rings in packings for control valves, reciprocating

metering pumps, or the like, where precise control is required.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1a illustrates a method of manufacture of a seal ring from flexible graphite foil with an amorphous carbon surface.

FIG. 1b is a perspective view of a seal ring of the invention.

FIG. 2 is a simplified cross-sectional view of a stuffing box incorporating seal rings of the invention.

#### DESCRIPTION OF THE INVENTION

Suitable coke forming organic materials as precursors to the amorphous carbon phase are organic materials capable of being coked, or those capable of forming amorphous carbon, when subjected to elevated temperatures. Examples include thermosetting and thermoplastic resins such as phenolic resins, prepolymerized furfuryl alcohol, and pitches. Preferred materials are those with high coke yield, greater than about 40 wt. %, such as phenolic-based thermosetting resins as used in the examples below, and pitches containing polynuclear hydrocarbons. In general, the organic material must be capable of being applied upon a surface of the flexible graphite article by any suitable method and capable of penetrating the surface. The organic material may be applied as liquid, or as solid particles which have been softened or liquefied by heat or a solvent to allow penetration, or applied dissolved in a liquid solvent and thereafter volatilizing the solvent.

A preferred method of applying the organic material is to sprinkle solid particles, such as a phenolic resin, upon the surface, and then spraying the surface with a solvent to soften and partially liquify the particles. Preferably, the surface of the flexible graphite article is embossed with small indentations to aid in dispersion of the solid particles over the surface. This can be accomplished during formation of the flexible graphite article by compressing the exfoliated graphite flakes with a device having a compression surface of coarse woven cloth, or the like, to emboss the surface of the compressed flexible graphite with uniform indentations.

If the organic material is a thermosetting resin, the resin may be optionally cured before the coking step. However, curing may not be required to obtain a satisfactory amorphous carbon phase.

The flexible graphite article may be further compressed. Preferably to a density less than 2.0 g/cm<sup>3</sup>, after application of the organic material, and after curing if a thermosetting resin is used, to provide more strength for further handling of the article. In addition, after coking of the organic material and after application of any lubricious material, the flexible graphite article is preferably further compressed to a final density between about 0.5 g/cm<sup>3</sup> and 2.0 g/cm<sup>3</sup>, preferably between about 0.8 g/cm<sup>3</sup> and 1.6 g/cm<sup>3</sup>.

The amorphous carbon phase is typically present in the article of the invention in an amount between about 0.1 to about 75 wt. % of the combined weight of the flexible graphite and the amorphous carbon. The exact weight depends in large part on thickness of the article and the proportion of the amorphous carbon surface to the total surface of the article. Too small an amount will not provide sufficient amorphous carbon phase upon the surface to provide suitable anti-chatter properties. Too large an amount will provide insufficient flexible graphite for the article to have adequate resiliency to

form a seal. The amount of amorphous carbon can be varied by altering the amount and type of organic material. For articles in the form of flexible graphite sheets less than about 20 mils (0.5 mm) thick with one amorphous carbon surface, the amount of amorphous carbon is typically between 10 wt. % and 25 wt. %, based on the total weight.

Suitable lubricious materials include any material with a lubricious property such as organic lubricants, in particular those comprising hydroxyl-containing polymers. Suitable lubricious materials include, for example, long chain alcohols, such as dodecanol, fatty acids and their iron derivatives, such as stearic acid, arachidic acid, ferric stearate, and iron arachidate, polyethers, polyethylene glycols, silicone oils (i.e. silicones), such as polydimethylphenylsiloxane, and fluorinated hydrocarbon polymers, such as polytetrafluoroethylene (PTFE). Preferred lubricious materials are PTFE and ferric stearate.

Liquid lubricious materials may be applied by painting, spraying, or any suitable technique. Solid lubricious materials may be applied as powder by sprinkling upon the article surface and heating to fuse or melt the material, or dissolving the lubricious material in a solvent, spraying or painting the solution over the surface, and volatilizing the solvent. For example, ferric stearate can be applied by sprinkling upon the surface and melting by heating to about 100° C. or above, or by dissolving the ferric stearate in toluene or carbon tetrachloride and painting or spraying the liquid solution upon the surface. In general, any coating method which applies a reasonably uniform layer is suitable.

The article of the invention is preferably an annular shaped seal ring wherein the cylindrical surface facing inwardly, the surface which is adapted to contact a stem, is the surface with the amorphous carbon phase. A seal ring may be made from a flexible graphite sheet made according to the invention with at least one surface with an amorphous carbon phase. Preferably, the surface has been treated with a lubricious material. The seal ring is produced by cutting a tape from the sheet and wrapping the tape around a shaft to produce an annular ring-shaped article with the tape arranged in a spiral fashion. To ease the rolling of the tape, the sheet is preferably previously compressed to a thickness of about 15 mils (0.38 mm) or less. The surface of the tape with the amorphous carbon phase is placed against the shaft such that the inner annular surface of the ring is the surface with the amorphous carbon phase. The resulting annular shaped article is then placed into a die mold and compressed to form a seal ring, preferably to a density between 1.3 g/cm<sup>3</sup> and 1.6 g/cm<sup>3</sup>.

Referring to FIGS. 1a and 1b, which illustrate a seal ring the invention produced in the manner described above. Referring to 1a, a flexible graphite tape 11 is wrapped around a shaft 13 in a spiral fashion to form an annular article 14. The flexible graphite tape 11 has an amorphous carbon surface 15 and is wrapped around the shaft 13 such that the amorphous carbon surface 15 is placed adjacent to the shaft 13. The thickness of the tape 11 in the figure is exaggerated for illustration purposes. The amorphous carbon surface 15 of the flexible graphite tape 11 may only correspond to that portion which is adjacent to the shaft, or the amorphous carbon surface 15 of the tape 11 may extend along its entire length such that its amorphous carbon surface 15 extends in a spiral 17 through the annular article 14, as illustrated.

Referring to FIG. 1b, the resulting article is compressed in a die to form an annular shaped seal ring 151 with an inner cylindrical surface 153 of amorphous carbon.

FIG. 2 illustrates the preferred use of the invention as a seal ring in a packing for a reciprocating shaft. Reciprocating stem 101 (as shown by the arrows 103) passes through an outer wall 105 of a fluid handling device 107, such as a control valve, through a first aperture 111 into a container means or stuffing box 109, and out of 10 the stuffing box 109 through second aperture 113. The stuffing box 109 contains a packing 115 comprising one or more seal rings 116 of the invention. A compression means, illustrated here as a threaded packing gland nut 119, is threaded down to compress the packing material 115, and conform the packing material 115 to the internal space of the stuffing box 109. The compression also forces the amorphous carbon surface 121 of the seal rings against the surface of the stem 11, forming a seal against the passage of fluid. Annular end rings 117 may be optionally placed around the stem 101 between the packing material 115, and each of the apertures 111, 113 to prevent extrusion of the seal rings 116 through the clearances 123 between the stem 101 and the edges of the apertures 111, 113, which results from compression 25 of the packing 115. The end rings may be of conventional design, such as end rings of braided carbon or graphite fibers, or may be end rings as disclosed in U.S. application Ser. No. 154,034 filed Feb. 9, 1988.

#### EXAMPLE I

This example illustrates production of a seal ring according to the invention.

Flexible graphite sheet is manufactured in the conventional manner by compressing exfoliated graphite flakes to a density of about 0.1 g/cm<sup>3</sup>. The surface of the compression device is covered with a coarse cloth to emboss the surface of the sheet with uniform indentations. A powdered phenolic resin is applied to the surface of the sheet and the excess not in the indentations is removed with a squeegee. The indentations are filled with the resin, which assists in an even dispersion of the resin over the sheet surface. The resin is a phenolic resin available from Union Carbide Corporation, Danbury, Conn., under the tradename BRP-5980.

The surface is then lightly sprayed with isopropyl alcohol to partially liquefy the resin and cause the resin to penetrate into the surface. The resin is then cured by heating the sheet at a rate of 10° C./hour from 25° to 50° C. with a one-hour hold at 175° C. The sheet is then further compressed to a density of 1 g/cm<sup>3</sup> and a thickness of 16 to 17 mils (0.41 to 0.43 mm). The cured resin is then carbonized to form an amorphous carbon phase by heating in a nitrogen atmosphere at a rate of 60° C./hour from 50° C. to 520° C. with a one-hour hold at 55 520° C. The sheet contains about 15 wt. % amorphous carbon, based on the total weight. The sheet is then compressed to a thickness of 15 mils (0.38 mm) and a density of about 1.1 g/cm<sup>3</sup>.

A seal ring is made from the sheet by cutting the sheet 60 into strips to form tape and wrapping the tape around a shaft to produce an annular ring-shaped article with the tape arranged in a spiral fashion. The amorphous carbon surface of the strip is placed against the shaft such that the inner annular surface of the ring is the amorphous carbon surface. The article is then placed into a die mold and compressed to a density of about 1.45 g/cm<sup>3</sup> to form a seal ring.

#### EXAMPLE II

This example illustrates production of a seal ring of the invention with a ferric stearate lubricious material applied to the amorphous carbon surface.

Flexible graphite sheet is manufactured in the conventional manner by compressing exfoliated graphite flakes to a density of about 0.1 g/cm<sup>3</sup>. The surface of the compression device is covered with a coarse cloth to emboss the surface of the sheet with uniform indentations. A powdered phenolic resin is applied to the surface of the sheet and the excess not in the indentations is removed with a squeegee. The indentations are filled with the resin, which assists in an even dispersion of the resin over the sheet surface. The resin is a phenolic resin available from Union Carbide Corporation, Danbury, Conn., under the tradename BRP-5980.

The surface is then lightly sprayed with isopropyl alcohol to partially liquefy the resin and cause the resin to penetrate into the surface. The resin is then cured by heating the sheet at a rate of 10° C./hour from 25° to 175° C. with a one-hour hold at 175° C. The sheet is then further compressed to a density of 1 g/cm<sup>3</sup> and a thickness of 16 to 17 mils (0.41 to 0.43 mm). The cured resin is then carbonized to form an amorphous carbon phase by heating in a nitrogen atmosphere at a rate of 60° C./hour from 50° C. to 520° C. with a one-hour hold at 520° C. The sheet contains about 15 wt. % amorphous carbon, based on the total weight.

30 Ferric stearate is applied on the surface in an amount of about 0.01 to 50, preferably about 15 wt. %, based on the weight of the sheet. The ferric stearate is applied by sprinkling the ferric stearate of the surface and heating to 100° C. to melt the ferric stearate and allow it to spread evenly over the surface of the sheet.

The graphite sheet which now has a surface with an amorphous carbon phase, the surface overlaid by a layer of ferric stearate, is compressed to a thickness of 15 mils (0.38 mm) and a density of about 1.1 g/cm<sup>3</sup>.

35 A seal ring is made from the sheets as described in Example I.

#### EXAMPLE III

This example illustrates production of a seal ring of 45 the invention with a polytetrafluoroethylene (PTFE) lubricious material applied to the amorphous carbon surface.

Flexible graphite sheet is manufactured in the conventional manner by compressing exfoliated graphite flakes to a density of about 0.1 g/cm<sup>3</sup>. The surface of the compression device is covered with a coarse cloth to emboss the surface of the sheet with uniform indentations. A powdered phenolic resin is applied to the surface of the sheet and the excess not in the indentations is removed with a squeegee. The indentations are filled with the resin, which assists in an even dispersion of the resin over the sheet surface. The resin is a phenolic resin available from Union Carbide Corporation, Danbury, Conn., under the tradename BRP-5980.

The surface is then lightly sprayed with isopropyl alcohol to partially liquefy the resin and cause the resin to penetrate into the surface. The resin is then cured by heating the sheet at a rate of 10° C./hour from 25° to 50° C. with a one-hour hold at 175° C. The sheet is then further compressed to a density of 1 g/cm<sup>3</sup> and a thickness of 16 to 17 mils (0.41 to 0.43 mm). The cured resin is then carbonized to form an amorphous carbon phase by heating in a nitrogen atmosphere at a rate of 60° C./hour from 50° C. to 520° C. with a one-hour hold at 520° C. The sheet contains about 15 wt. % amorphous carbon, based on the total weight.

60° C./hour from 50° C. to 520° C. with a one-hour hold at 520° C. The sheet contains about 15 wt. % amorphous carbon, based on the total weight.

PTFE is applied as a dispersion in water, (available as Teflon® T30 from DuPont de Nemours, Wilmington, Del.) by spraying the dispersion upon the surface in an amount of 0.1 to 50, preferably 5 wt. % PTFE, based upon the total weight of the PTFE and article. The sprayed article is then quickly heated to 500° F. (260° C.) to fuse the PTFE.

The graphite sheet which now has a surface with an amorphous carbon phase, the surface overlaid by a layer of PTFE, is compressed to a thickness of 15 mils (0.38 mm) and a density of about 1.1 g/cm<sup>3</sup>.

A seal ring is made from the sheet as described in Example I.

#### EXAMPLE IV

Seal rings were produced as described in Examples I, II, and III, and tested. The ferric stearate-treated rings contained 15 wt. % ferric stearate, and the PTFE treated rings contained 5 wt. % PTFE. Comparative seal rings were made by wrapping tapes cut from untreated conventional flexible graphite sheet (density 1.4 g/cm<sup>3</sup>) around a shaft and compressing in a die as described in

#### Example I.

The rings were tested upon a test fixture comprising a stuffing box, stem, and stem actuator combination of a conventional valve. Instead of a complete valve assembly, the combination is attached to a pressure vessel. The pressure vessel was pressurized to 750 psig (5.7 MPa gauge) with dry nitrogen gas, and the actuator cycled the stem back and forth through the packing from one end of the stem, with the other end of the stem in the pressure vessel. The packing comprised six rings installed in the stuffing box in the conventional manner. The dimensions of the rings were; outside diameter, 1 1/8 inches; inside diameter 1 1/8 inches; and thickness, 1/4 inch (41.3 mm × 28.6 mm × 6.4 mm). Each test was run for 5000 cycles over about a five hour period. During each test, any chatter, squeaking noise, or leakage around the stem was observed. The results are summarized in Table A.

TABLE A

Seal Ring Chatter Properties	
Seal Ring	Observation
Comparative	Very Bad Chatter
Amorphous Carbon (AC) Surface	Slight Chatter
AC Surface with Ferric Stearate	No Chatter
AC Surface with PTFE	No Chatter

The above results demonstrate the dramatic chatter reduction that can be achieved by practice of the invention.

#### EXAMPLE V

Flexible graphite seal rings with surfaces of various compositions were produced and tested for chatter reduction. The surface materials were chosen from materials generally recognized as having a lubricious surface. The seal rings were dimensioned as in Example IV and tested as in Example IV for chatter. The surface material and the results of the tests are shown in Table B. The ZnCl/BN and pyrolytic graphite surfaced rings (A and B) were formed by pressing powders into the surface of a flexible graphite sheet and forming seal

rings by wrapping strips of the sheet around a shaft and compressing into seal rings as previously described.

Composite coated rings (C, D, and E) were formed by applying a paste of a phenolic thermosetting resin binder and a filler of carbon fibers, coke flour, or lampblack upon the surface of a flexible graphite sheet, and carbonizing the resin. The resulting surface comprised discrete carbon particles bound together and to the surface of the sheet by the carbonized phenolic binder, with negligible penetration of amorphous carbon into the interior of the sheet. Strips of the sheet were then wound around a shaft and compressed into seal rings as previously described.

TABLE B

Comparative Seal Ring Surfaces		
Ring	Surface Material	Observation
A	Zinc Chloride & Boron Nitride	Very Bad Chatter
B	Pyrolytic Graphite	Very Bad Chatter
C	Carbon Fibers	Very Bad Chatter
D	Coke Flour	Very Bad Chatter
E	Lampblack	Very Bad Chatter

In summary, chatter reduction by the tested seal rings was negligible or nonexistent. In addition to the very bad chatter, the seal ring with ZnCl/BN surface (A) caused corrosion on the stem, and the seal ring with the coke flour surface (D) leaked during the test.

This test demonstrates, that even when surfaces that would be expected to be low friction surfaces are applied to seal rings, there is little or no reduction in the chatter.

While this invention has been described with reference to certain specific embodiments and examples, it is recognized by those skilled in the art that many variations are possible without departing from the scope and spirit of the invention, and that the invention, as described by the claims, is intended to cover all changes and modifications which do not depart from the spirit of the invention.

What is claimed is:

1. A method for manufacturing a flexible graphite article for use as a seal comprising:
  - (a) compressing exfoliated graphite flakes into an article having a density between 0.05 g/cm<sup>3</sup> and 2.0 g/cm<sup>3</sup>;
  - (b) applying a material composed of coke forming organic constituents upon a predetermined surface of said sheet; and
  - (c) subjecting the article to a temperature sufficient to carbonize said coke forming organic constituents to form a continuous amorphous carbon phase extending from said predetermined surface of the article only partially into the interior of said sheet.
2. The method of claim 1 wherein in step (a) the exfoliated graphic flakes are compressed to a density between 0.05 g/cm<sup>3</sup> and 1.5 g/cm<sup>3</sup>.
3. The method of claim 1 wherein in step (a) the exfoliated graphic flakes are compressed to a density between 0.1 g/cm<sup>3</sup> and 0.5 g/cm<sup>3</sup>.
4. The method of claim 1 wherein the article is further compressed to a density between 0.5 g/cm<sup>3</sup> and 2.0 g/cm<sup>3</sup> after step (c).
5. The method of claim 1 wherein the article is further compressed to a density between 0.8 g/cm<sup>3</sup> and 1.5 g/cm<sup>3</sup> after step (c).

6. The method of claim 1 additionally comprising the step of (d) applying a lubricious material upon the surface with the amorphous carbon phase.

7. The method of claim 6 wherein the lubricious material is an organic lubricant.

8. The method of claim 7 wherein the organic lubricant is hydroxyl-containing.

9. The method of claim 6 wherein the lubricious material is chosen from the group consisting of long chain alcohols, fatty acids, iron derivatives of fatty acids, polyethers, polyethylene glycols, silicone oils, and fluorinated hydrocarbon polymers.

10. The method of claim 6 wherein the lubricious material is ferric stearate.

11. The method of claim 6 wherein the lubricious material is polytetrafluoroethylene.

12. A flexible annular-shaped seal ring adapted to provide a seal around a moving shaft comprising a thin resilient sheet of compressed exfoliated flakes of graphite having a density between 0.05 g/cm<sup>3</sup> and 2.0 g/cm<sup>3</sup> and a thin layer comprised substantially or entirely of carbonized resinous organic material defined by a continuous amorphous carbon phase extending from a predetermined surface of said sheet only partially into the interior of said sheet for directly engaging said shaft to form a compressible seal.

13. The seal ring of claim 12 wherein the seal ring comprises between 0.1 and 75 weight percent of the amorphous carbon phase, based on the total weight of the ring.

14. The seal ring of claim 12 wherein the seal ring comprises between 10 and 25 weight percent of the amorphous carbon phase, based on the total weight of the ring.

15. The seal ring of claim 12 wherein the density of the seal ring is between 0.5 g/cm<sup>3</sup> and 2.0 g/cm<sup>3</sup>.

16. The seal ring of claim 12 wherein the density of the seal ring is between 0.8 g/cm<sup>3</sup> and 1.6 g/cm<sup>3</sup>.

17. The seal ring of claim 12 wherein a lubricious material is present upon the inner cylindrical surface.

18. The seal ring of claim 17 wherein the lubricious material is chosen from the group consisting of long chain alcohols, fatty acids, iron derivatives of fatty acids, polyethers, polyethylene glycols, silicone oils, and fluorinated hydrocarbon polymers.

19. The seal ring of claim 18 wherein the lubricious material is ferric stearate.

20. The seal ring of claim 18 wherein the lubricious material is polytetrafluoroethylene.

21. The seal ring of claim 12 wherein the lubricious material is an organic lubricant.

22. The seal ring of claim 21 wherein the lubricious material is hydroxyl-containing.

23. A seal adapted to prevent fluid leakage through the clearance between a stem and the edge of an aperture where the stem passes through the aperture in a wall which comprises:

(a) container means disposed upon the wall and around the shaft and around the aperture in the wall;

(b) at least one annual-shaped seal ring comprising flexible graphite, the seal ring having a inner cylindrical surface adjacent to the stem with a cured coating comprised of carbonized resinous organic material having a continuous amorphous carbon phase extending from said surface only partially into the interior of the seal ring; and

(c) compression means for compressing the seal ring

in the direction of the stem axis to cause the car-

bonized coating on the inner cylindrical surface of

the seal ring to bear against the stem surface to

provide a seal.

24. A method for manufacturing a flexible graphite seal ring having an inner cylindrical surface adapted to provide a seal around a stem with a continuous amorphous carbon phase upon the inner cylindrical surface extending from said surface only partially into the interior of the seal ring, the method comprising:

(a) compressing exfoliated graphite flakes into an article having a density between 0.05 g/cm<sup>3</sup> and 2.0 g/cm<sup>3</sup>;

(b) applying a material composed of coke forming organic constituents upon at least one surface of the sheet; and

(c) subjecting the sheet to a temperature sufficient to carbonize said coke forming organic constituents to form said amorphous carbon phase extending from the surface of the sheet only partially into the interior of said sheet;

(d) wrapping the sheet about a shaft to form an annular shaped article with a portion of the amorphous carbon surface adjacent to the shaft; and

(e) compressing the annular shaped article to form an annular shaped seal ring with an inner cylindrical surface adapted to provide a seal around a stem, the inner surface having an amorphous carbon phase.

25. The method of claim 24 wherein the annular shaped article is compressed in (e) to form a seal ring with a density between 1.3 g/cm<sup>3</sup> and 1.6 g/cm<sup>3</sup>.

UNITED STATES PATENT AND TRADEMARK OFFICE  
CERTIFICATE OF CORRECTION

PATENT NO. : 5,228,701

DATED : July 20, 1993

INVENTOR(S) : R.A. GREINKE ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col. 1, line 50, change "such as water. Petro-" to --such as water, petro--

Col. 2, line 20, after "preferably" delete "g/cm<sup>3</sup>"

Col. 9, line 26, after "in" insert --Example I.--

Col. 9, line 28, delete "Example I."

Col. 10, line 45, delete "an"

Col. 10, line 46, change "article" to --a thin sheet--

Col. 11, line 44, change "chosen" to --selected--

Col. 12, line 30, delete "an"

Col. 12, line 31, change "article" to --a thin sheet--

Col. 12, line 35, delete "and"

Signed and Sealed this  
Fifth Day of April, 1994



Attest:

Attesting Officer

BRUCE LEHMAN

Commissioner of Patents and Trademarks

12/25/84

XR 4,490,201

**United States Patent [19]**  
**Leeds**

[11] Patent Number: **4,490,201**  
[45] Date of Patent: **Dec. 25, 1984**

[54] **METHOD OF FABRICATING CARBON COMPOSITES**

[75] Inventor: Donald H. Leeds, Rolling Hills, Calif.

[73] Assignee: The B. F. Goodrich Company, Akron, Ohio

[21] Appl. No.: **291,309**

[22] Filed: **Aug. 10, 1981**

[51] Int. Cl.<sup>3</sup> ..... **B32B 31/20**

[52] U.S. Cl. .... **156/155; 156/256;**  
**156/307.3; 156/330; 156/330.9; 156/335;**  
**156/336; 264/29.5; 264/29.6; 264/29.7;**  
**423/447.1; 423/447.2; 423/447.4; 427/228;**  
**427/249; 428/262; 428/287; 428/408; 428/902**

[58] Field of Search ..... **156/155, 307.3, 256,**  
**156/330, 330.9, 335, 336; 423/447.1, 447.2,**  
**447.4; 264/29.1, 29.5, 29.6, 29.7; 427/228, 249;**  
**428/196, 198, 260, 262, 280, 287, 288, 289, 408,**  
**902**

[56] References Cited

U.S. PATENT DOCUMENTS

4,029,829 5/1977 Weaver et al. .... 427/249 X  
4,234,650 11/1980 Schieber ..... 264/29.7 X

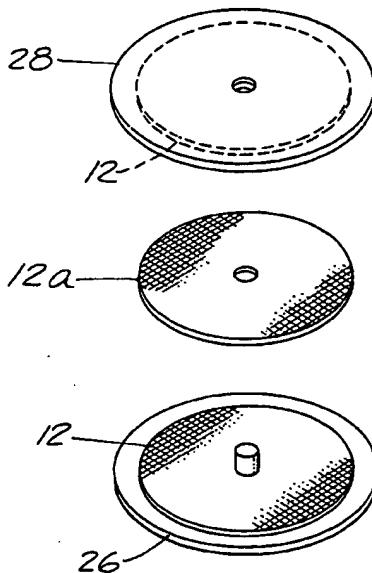
Primary Examiner—Robert A. Dawson  
Attorney, Agent, or Firm—James E. Brunton

[57] ABSTRACT

An improved method of making a carbon composite product wherein a fabric comprised of oxidized or oth-

erwise stabilized polyacrylonitrile fibers is heat treated and then coated with a closely controlled amount of a carbonaceous binder such as a polyimide resin. The fabric is then further heat treated to thermally fuse the resin to the fabric to form a rigid, easily handleable material. The carbonaceous binder is applied to the fabric in a manner whereby substantial encapsulation of the individual fibers is avoided. Next the material is cut into swatches of a predetermined size and shape and the segments are arranged into a basic or starting substrate having a volume greater than the desired volume of the end product. The basic substrate thus formed is then subjected to controlled temperatures and pressures to form a shaped substrate having a known fiber volume, a high degree of open porosity and a shape substantially corresponding to the shape desired of the end product. During this step, the fiber volume of the substrate is adjusted and the segments are fused together to temporarily hold them in position within the substrate. The shaped substrate thus formed is then pyrolyzed to form a carbon fibrous substrate which is densified in a free-standing configuration by the deposition of pyrolytic carbon interstitially thereof to form the desired end product. Because the portions of the fibers which are not encapsulated with binder are free to move, stresses generated in the substrate during pyrolyzation due to material shrinkage and the like are effectively distributed.

10 Claims, 4 Drawing Figures



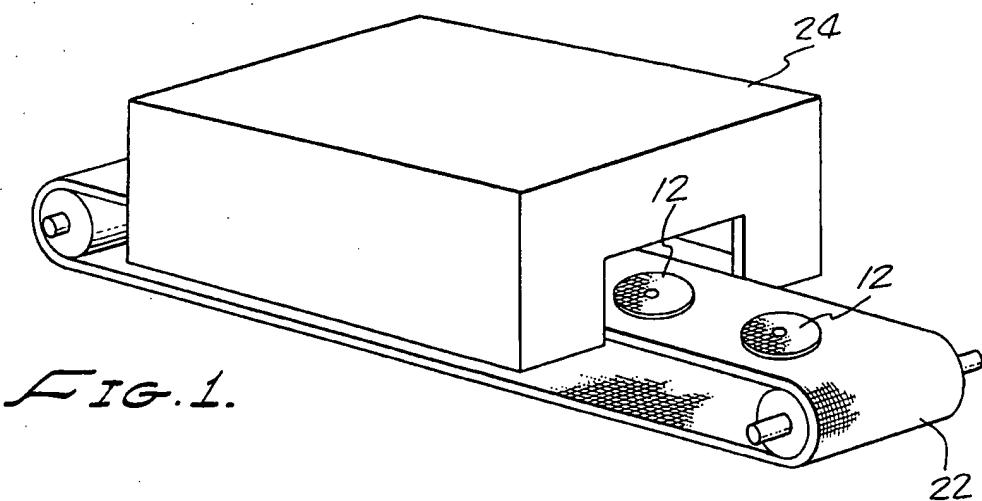


FIG. 1.

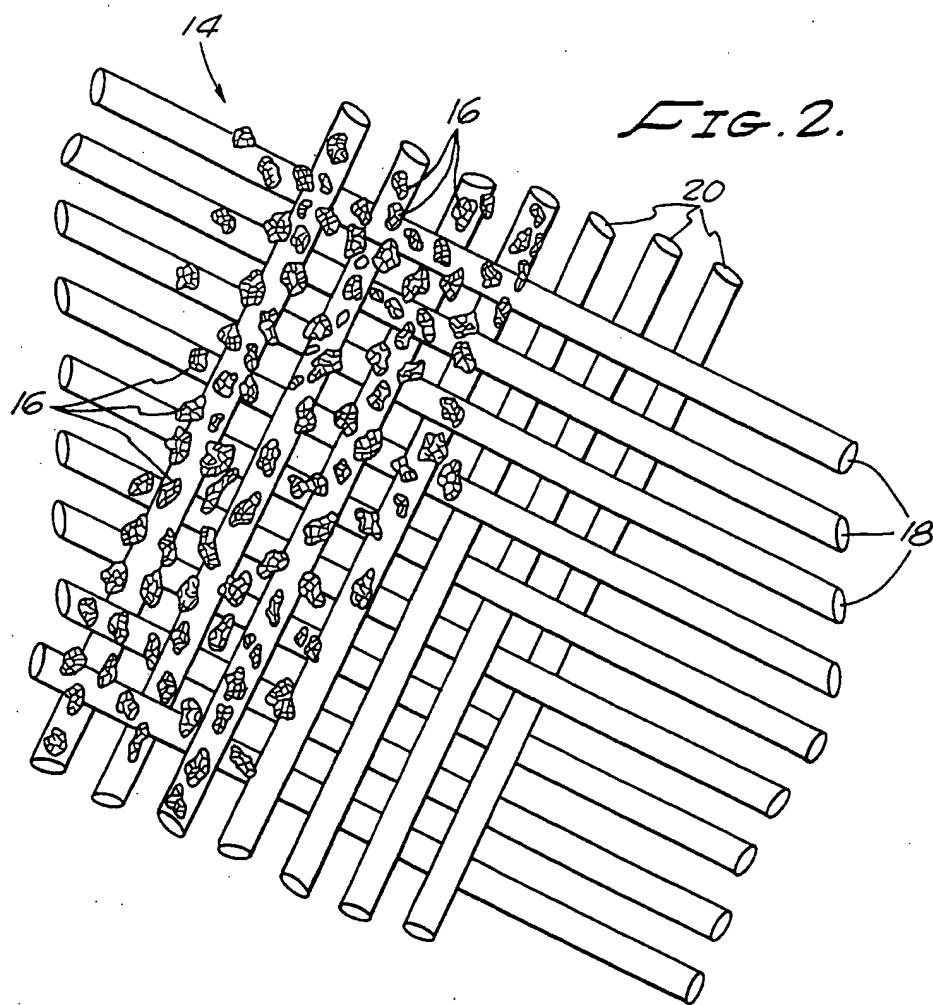


FIG. 2.

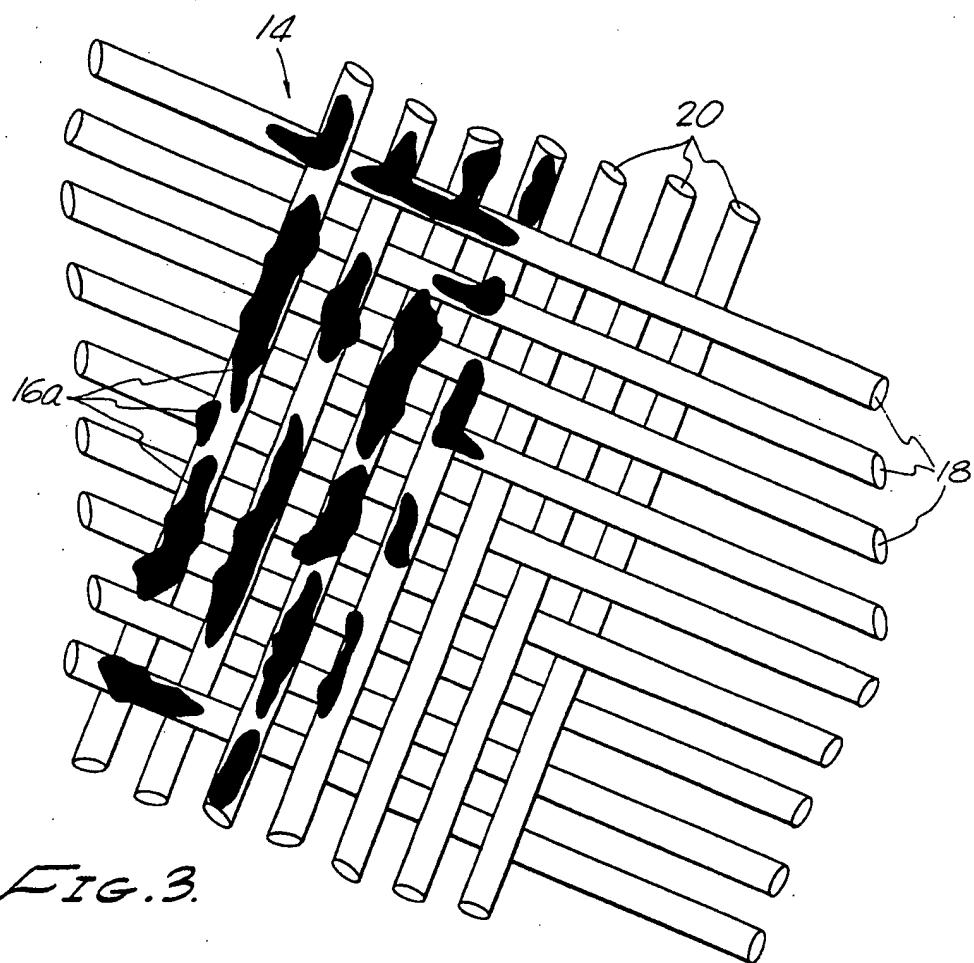


FIG. 3.

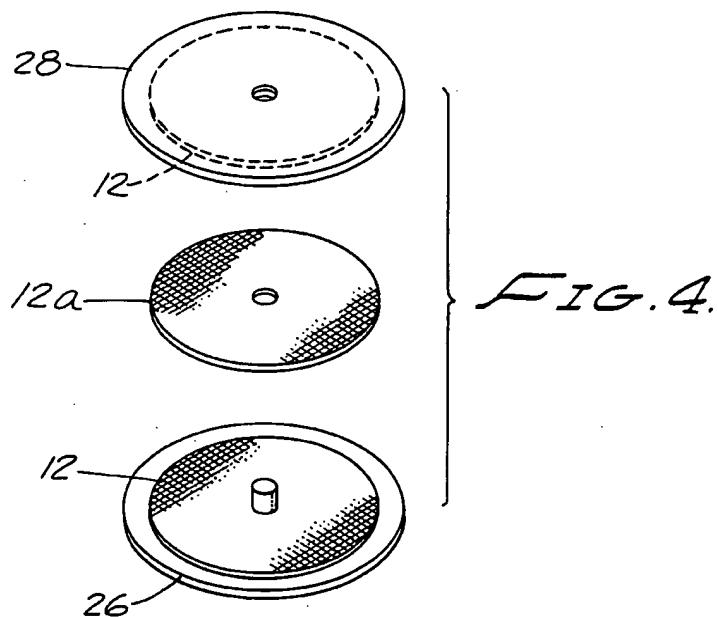


FIG. 4.

## METHOD OF FABRICATING CARBON COMPOSITES

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates generally to methods of making carbon composite articles. More particularly, the invention relates to a novel process wherein a porous, rigidized shaped substrate, or preform, is constructed from layers of an interwoven fibrous fabric material which has been heat treated and onto the fibers of which has been thermally fused a very small amount of a carbonaceous binder. To complete the composite product, the substrate is subjected to controlled conditions of temperature and pressure and then is controllably densified by the chemical vapor deposition of pyrolytic material interstitially thereof.

#### 2. Discussion of the Prior Art

Excellent high temperature performance characteristics of carbon composites in structural, frictional, ablative and thermal insulation applications has caused an ever expanding demand for such materials. Accordingly considerable effort has been extended in recent years in developing new techniques for the large scale production of such materials for use in nuclear, aerospace, aircraft and industrial fields.

In producing carbon composite products, substrates or preforms, made up of carbon fibrous materials are first constructed. Two basic methods are typically employed to produce the substrates. In accordance with one method, sometimes called the resin bonding method, the fibrous substrate materials are bonded together using substantial amounts of carbonizable binder such as phenolic resin or the like. The methods described in the patent to Bickerdike et al, U.S. Pat. No. 3,233,014 is exemplary of the resin bonding method. In accordance with the second method, often called the Chemical Vapor Deposition or C.V.D. method, the fibrous substrate materials are bonded together by the interstitial deposition of pyrolytic carbon using known chemical vapor deposition (C.V.D.) techniques. The patent to Bauer, U.S. Pat. No. 3,895,084, clearly describes the C.V.D. method. Also pertinent to this method is the British patent to Williams, U.S. Pat. No. 1,455,891.

The resin, or carbonaceous binder method has certain recognized advantages. For example, using this method, durable, high density structurally stable preforms can readily be produced using conventional molding and press bonding techniques. The preforms formed by this method can conveniently be shaped and are easily handleable. Drawbacks of the resin binder method, however, include the fact that the method is relatively expensive requiring several preparatory processing steps including pre-impregnation of the substrate materials, "B" staging and binder carbonization. Additionally, difficulties have been experienced using this method in achieving acceptable compatibility between fiber and binder processing shrinkages, and in routinely producing preforms which retain acceptable part integrity during the various substrate processing steps without delaminating or micro-cracking. In a similar vein, the relatively high quantities of carbonizable binder necessary to produce an acceptable carbonizable substrate frequently pose debulking, outgassing and dimensional stability problems during carbonization of the binder. A frequent objective of the resin bonding method is to

totally encapsulate the individual fibers of the substrate in an attempt to eliminate undesirable voids in the substrate.

The C.V.D. method, wherein substrate bonding is accomplished by depositing onto the fibers of the substrate carbon resulting from dissociating methane or other carbon bearing source gasses, also has several recognized advantages. For example, this technique produces a substrate having maximum open porosity so as to permit precisely controllably partial or complete substrate densification. Additionally, inherent in the method is the fact that each fiber of the substrate is uniformly coated with the deposited material rendering it substantially impermeable and unusually resistant to corrosion even at high temperatures. Further, the thickness of the coating on the fibers themselves and at the fiber cross-over points can be precisely regulated so as to achieve the desired substrate rigidity.

A major disadvantage of the C.V.D. method is that some form of expensive and often bulky shaping fixture is required to hold the substrate materials in the desired configuration until sufficient pyrolytic carbon has been deposited to rigidize the fibrous structure. Such hardware is expensive, reduces furnace productivity substantially since it occupies a significant portion of the severely limited furnace processing volume, and presents significant assembly and disassembly problems.

As will become apparent from the discussion which follows, the method of the present invention permits realization of the advantages of both the resin and C.V.D. methods while substantially avoiding the disadvantages of each method.

A method devised to attempt to overcome the problem of clogging the interstices of the substrate with resin is described in co-pending U.S. application Ser. No. 047,158, now abandoned, wherein the present inventor is named as a co-inventor. The drawbacks of the method described in said application relate to difficulties encountered in precisely controlling the amount of resin used as a temporary bonding agent and in handling the fabrics to which the resin is applied. In the process of the previously described invention the resin impregnated fabric is fragile and difficult to handle and cut. Additionally, during handling, the resin applied to the material tends to powder and spall making precise control of the amount of resin contained in the shaped substrate impossible. The method of the present application uniquely and effectively solves this problem in a way which enables large volume production of the starting substrate material.

In addition to the prior art identified in the preceding paragraphs, applicant is aware of a printed publication entitled "Development of High Modulus Carbon Fiber Tape Composites" published by United Technology Laboratories which describes methods of making composite articles using carbon fiber tape.

### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a novel method of making a carbon composite product in which a precursor substrate is constructed from interwoven oxidized, stabilized PAN fibers which have been coated with a very small amount of binder such as a polyimide resin. The precursor substrate is then compressed under controlled conditions of temperature and pressure to form a shaped substrate, the individual fibers of which are temporarily bonded together. Due to the

small amount of resin used, the interstices of the shaped substrate remain open to permit free interstitial deposition of a pyrolytic material which permanently bonds the fibers together to form a rigid article of known density.

It is another object of the invention to provide a method of the aforementioned character in which the fibers of the shaped substrate are sufficiently bonded together to permit the substrate to be freely handled during the pyrolyzation and densification steps of the process without the need for holding fixtures or other means of constraining the shape of the substrate.

Another object of the invention is to provide a method as described in the preceding paragraphs in which substantial encapsulation of the fibers within the binder material is carefully avoided so that the portions of the individual fibers are free to move to accommodate and distribute stresses generated within the substrate due to material shrinkage and other process related causes.

It is another object of the invention to provide a novel method for the construction of shaped substrates of the class described in which various carbonaceous binder materials can be used including polysaccharides and phenolic, polyimide, polyamide, furfural or pitch resins.

It is yet another object of the invention to provide a method of the character described in the preceding paragraphs in which the carbonaceous binder material is safely carbonized during the densification step thereby eliminating the need for a special binder carbonization step.

It is a further object of the invention to provide a method of the aforementioned character in which partially carbonized, fully carbonized, or graphitized fibrous substrate materials can be used without the necessity of matching volumetric shrinkages of the fibers and carbonaceous binders to achieve acceptable precursor substrates.

Another object of the invention is to provide a method of making carbon composites in which, by carefully controlling the amount of binding material used to coat the fibers of the starting material, the binder will not adversely effect the densification process, nor will it result in structural defects in the finished article.

A further object of the invention is to provide a method of making carbon composites in which the binding material may be precisely deposited in known amounts onto the fibers of the fabric material in liquid or particulate form.

Still another object of the invention is to provide a method of making carbon composites in which the resin can be thermally fused to the fibers of the starting material in a cost effective, continuous, or semi-continuous process thereby enabling high volume production of carbon composite articles of precise shape, density and fiber volume.

Another object of the invention is to provide a method of making carbon composites in which the resin applied to the starting fabric is thermally fused to the fibers thereof to rigidize the fabric and make it easy to handle and to form into segments of precise weight and dimension.

Finally it is an object to provide a final composite article of the aforementioned character having superior mechanical properties including high interlaminar shear strength, high edge flex strength and high flat flex strength after full CVD densification.

In summary, these and other objects of the invention are achieved by a novel method comprising the steps of heat treating a two dimensional agglomeration of stabilized PAN fibers; coating the fibers with a predetermined amount of carbonaceous binder; further heat treating the material thus formed to thermally fuse the binder to the individual fibers; cutting the treated agglomeration of fibers (woven into fabric or nonwoven into mats) into segments of a predetermined size and shape; arranging the segments into a basic substrate having a volume greater than the volume of the end product; compressing the basic substrate at a temperature of between approximately 300° F. and approximately 410° F. into a shaped substrate having a known volume and a shape substantially corresponding to the shape desired of the end product; pyrolyzing the shaped substrate to form a carbon fibrous substrate; and maintaining the carbon fibrous substrate in the presence of a carbonaceous gas at a temperature of between approximately 1900° F. and approximately 2300° F. to deposit pyrolytic carbon interstitially in said carbon fibrous substrate.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view illustrating the method of thermally fusing the carbonaceous binder material onto the fibers of the shaped segments used to construct the basic substrate.

FIG. 2 is a greatly enlarged, fragmentary view of a portion of a woven fibrous material made up of warp and fill yarns onto which particles of a carbonaceous binder material have been selectively deposited.

FIG. 3 is a greatly enlarged, fragmentary view of the portion of material shown in FIG. 2 illustrating its appearance after the material has been processed through the oven processing step illustrated in FIG. 1 wherein the binder material is thermally fused to the individual fibers of the shaped segments.

FIG. 4 is a perspective, exploded view illustrating the method of assembly of the coated swatches onto pressing plates used in the construction of the basic substrate.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Before proceeding with a detailed discussion of the preferred embodiments of the present invention, the following definitions of the technical terms used herein are presented to facilitate a clear understanding of the nature and scope of the invention:

1. Carbon composite product—a product consisting of a fibrous material, the fibers of which are intertwined in woven (fabrics) and non-woven (mats) and are oxidized stabilized, partially carbonized, fully carbonized or graphitized, a carbonaceous binder material and a pyrolytic material deposited interstitially of the fibrous material.
2. Basic or precursor substrate—as used herein, the starting substrate or interim product shape before compressing the substrate into a shaped substrate.
3. Shaped substrate or preform—the pressed or formed basic substrate suitable for pyrolysis or densification with pyrolytic material.
4. Carbon fibrous substrate—the shaped substrate after pyrolysis ideally suited for interstitial deposition of pyrolytic carbon or a similar material.
5. Carbon fiber—carbon material in fibrous form.
6. Carbonaceous binder—a material adapted to be thermally fused to the fibers of the woven starting

material at selected bonding sites without encapsulating a substantial portion of the fiber. Various resin materials including thermoplastic resins have proven satisfactory as the binder material.

7. Pyrolytic material—the material formed by pyrolysis, that is chemical decomposition by heat. Various pyrolytic materials may be used in the densification step such as pyrolytic carbon, certain nitrides such as boron nitride, certain refractory metals such as tantalum, tungsten, molybdenum and columbium, as well as certain carbides including tantalum carbide, niobium carbide, zirconium carbide, hafnium carbide and silicon carbide.

8. Carbonaceous gas—a carbon containing gas.

9. Polyacrylonitrile (PAN) fibers—synthetic polymeric fibers.

10. Oxidized, or otherwise stabilized polyacrylonitrile fibers—black fibers formed by suitable oxidation or other chemical modification of polyacrylonitrile fibers under tension.

11. Fiber volume—volume of fibers present in the given substrate.

12. Woven—fabric formed by interlacing warp and filling threads on a loom, or the like.

13. Swatch—piece of woven or non-woven material used in manufacturing as a unit.

As will be clearly illustrated by the examples which follow, the method of the invention stated in simple terms comprises the following steps: First, a starting material in the form of intertwined PAN, rayon or wool fibers is heat treated to about 1600° C. Next, a small quantity of a suitable carbonaceous binder such as phenolic resin, polyimide resin, or a like material is applied to a selected carbon fibrous material. The binder can be applied to the material by hand sprinkling, through use of a roller brush, by surface spraying, or by other similar means. Next, the coated starting material is exposed to elevated temperatures for a controlled period of time to thermally fuse the resin to portions of the individual fibers. This is done in such a manner as to avoid total encapsulation of the fibers. The material thus formed, which is rigidized and easy to handle, is then assembled into a basic or starting substrate having a volume greater than the volume of the end product. The basic substrate is then subjected to controlled temperatures and pressures to form a shaped substrate which has a high degree of open porosity, a known volume and a shape substantially corresponding to the shape of the desired end product. During this "press bonding" step the individual fibers of the carbon fibrous material are selectively bonded together by the binder material at multiple sites. These bonds or "tacks" rigidize the substrate so that during the subsequent processing steps it can be readily handled in a free standing configuration. Finally, the shaped substrate or preform is partially, or fully densified in a freestanding configuration by chemical vapor deposition of selected pyrolytic materials interstitially of the substrate. The various pyrolytic materials which may be used are set forth in the examples which follow.

Depending upon the particular starting material and binder used, an interim carbonization step may be required. This carbonization step precedes the densification step and functions to controllably carbonize the binder and, in some instances, the fibers which make up the basic substrate. Additionally, for some applications either an interim or final heat treating step is undertaken.

Referring to the drawings, and particularly to FIG. 1, the method of the present invention comprises the steps of first cutting a carbon fibrous fabric material having a multiplicity of intertwined fibers into pieces having a predetermined size and shape. The material may be constructed from fibers of wool, rayon, polyacrylonitrile (PAN) or like materials and may be cut into annular shapes 12 of the character shown in FIG. 1, or into pie shaped segments, rectangles or other suitable configurations. The shape of the fabric "lay ups" is, of course, governed by the desired shape and end use of the final product being fabricated.

The next step in the method of the invention is to selectively deposit onto the fibrous material a very small quantity of a carbonaceous binder. Depending again upon the end use of the final product and the desired method of application of the binder, the carbonaceous binder material used may be a phenolic resin, a particulate polyimide resin such as "Kerimid 601" distributed by Rhodia, Inc. of New Brunswick, N.J., a furfural resin such as "Karbon 700R" distributed by Fiberite, Inc. of Winona, Minn., or various other binder materials well known to those skilled in the art.

The binder material may be diluted with a solvent such as isopropyl alcohol and then sprayed onto the fibrous material, or it may be sprinkled onto the fibrous material by hand or through the use of various types of mechanical dispensing apparatus.

Turning to FIG. 2, there is schematically illustrated in greatly enlarged perspective, a fabric material 14 such as PAN 8 harness satin manufactured by Stackpole Fibers, Inc. as it appears after a limited quantity of particulate binder material 16 has been deposited thereon. It is to be observed that the fabric material is made up of warp yarns 18 and fill yarns 20 which are interwoven together to form the fabric. Only a limited amount of binder is deposited on the fabric surfaces at spaced apart bonding sites along the warp and fill yarns. Great care is exercised in depositing the binder material to make certain that during subsequent heating steps, substantial encapsulation of the individual fibers will not occur. This is necessary to that the portions of the fibers which intermediate the bonding sites will be free to move to accommodate and effectively distribute stresses which may be generated during subsequent processing steps.

After depositing the carbonaceous binder onto the lay-ups 12, they are placed on a metal mesh conveyor belt 22 (FIG. 1) and are passed through a temperature controlled oven 24 at a fixed rate of speed. Oven 24 is of standard construction and may be heated electrically or by natural gas. The oven temperature and the speed of travel of the conveyor belt is, of course, varied depending upon the type of binder being used and the character of the starting material. Ideally, the material is exposed to the lowest temperature possible for the minimum time necessary to thermally fuse the binder to the fibers of the lay-ups. Exemplary time-temperature ranges are set forth in the examples which follow.

For certain large volume processing applications it may be desirable to cut the starting material into long sheets or ribbons, coat the material with the binder in the manner previously discussed and then continuously pass the material through the oven at a controlled rate of speed. The material thus formed can then be automatically cut into segments of a desired size and shape for further processing.

The appearance of the material after oven processing is illustrated in FIG. 3. As there shown the carbonaceous binder 16 has become thermally fused to the upper surfaces of the fibers at locations intermittent along their length. After fusion the binder takes on a smooth glassy like appearance as indicated by the numeral 16a in FIG. 3. Importantly, none of the fibers have been totally encapsulated with the fused binder so that portions of the fibers will be free to move to accommodate stresses generated within the material during subsequent processing. This approach is, of course, in direct contradistinction to the teaching of the prior art wherein complete encapsulation of the yarns of the fabric is deemed highly desirable in the fabrication of composite articles.

The coated fabric formed by the oven processing step is ideally suited for further processing. It is quite rigid and can be readily cut, shaped and easily transported. Also of significant importance is that the coated fabric exhibits no spalling or flaking of the binder material during handling. Accordingly, the amount of binder present in the finished article can be precisely determined and accurately controlled. This critical feature of the method of the present invention was unattainable in the previously devised methods discussed in the application earlier filed by applicant.

Referring now to FIG. 4, the next step in the method of the invention is to construct a basic substrate from the lay-ups 12 upon which the binder material has been thermally fused. In the form of the invention shown in FIG. 1 this is accomplished by first placing a lay-up 12 onto a large metal plate 26. Lay-up or disc 12 is free of binder material so as to facilitate separation of the substrate from the plate 26. Subsequent discs designated as 12a in FIG. 4, upon which the binder has been thermally fused, are then placed over disc 12 in a predetermined orientation, with a rotational offset from the preceding layer. After a predetermined number of layers of the coated fabric material have been assembled, a second binder free disc 12 is placed over the upper most piece of material and a second metal plate 28 is placed on top of the assembly.

The basic substrate thus formed, along with the metal plates 26 and 28, are placed into a press which is provided with heated press platens. The press and press platens used in the forming of the spaced substrate is of standard design and its construction and operation need not be described in detail herein.

The basic substrate is carefully constructed so that it has a volume greater than the desired volume of the final product, has a known fiber volume and contains a predetermined, limited amount of binder material. The actual fiber volumes and binder weight percent ranges used in the practice of the invention are illustrated in the examples which follow.

In forming the shaped substrate, the basic substrate is subjected to controllable external pressures of up to 5000 psi at predetermined temperature ranges of up to several hundred degrees Fahrenheit. The shaped substrate formed in accordance with the methods of the invention has a known volume, a known fiber volume, and has a shape substantially corresponding to the shape desired of the final product. The various temperature and pressure ranges actually used in the shaping step are illustrated in the examples which follow and are selected so as to controllably compress the basic substrate a predetermined amount and to cause the individual

fibers thereof to be bonded together at the multiplicity of spaced apart bonding sites.

Following the shaping step, the shaped substrate is removed from the metal plates and is placed in a free-standing configuration into a vacuum deposition furnace for densification with a selected pyrolytic material such as pyrolytic carbon. The densification is accomplished by well known chemical vapor deposition (CVD) techniques. The various temperature and pressure ranges suitable for the CVD densification step are set forth in the previously identified British Pat. No. 1,455,891.

Because the fibers of the shaped substrate are selectively bonded together by the binder material at a multiplicity of spaced apart bonding sites, the shaped substrate is suitably rigid to retain its shape during the densification step without the necessity of using bulky holding fixtures to constrain it in the desired configuration. This permits maximum use of valuable furnace space and constitutes a significant cost saving over typical prior art furnace processing methods. Additionally, and most importantly, because the individual fibers are not encapsulated in the binder material, the portions thereof which are disposed intermediate the bonding sites are free to flex and move to accommodate and distribute external stresses. Accordingly, no special matching of the binder matrix to fiber volumetric shrinkages is required to produce defect free fully or partially densified end products. Such a unique and important result is nowhere described nor suggested in the prior art.

During the CVD densification step, the binder material within the shaped substrate is fully carbonized. Simultaneously, the transient binder material fibers bonds are augmented by permanent fibers bonds formed by the pyrolytic material which has been deposited interstitially of the substrate.

#### Examples Illustrating Several Methods of the Invention

##### EXAMPLE NO. 1

A sample of woven fabric 44 inches wide by 22 inches long was heat treated at about 1600° C. in a manner well known to those skilled in the art. After heat treatment, an even thickness dry coating containing 28 weight percent of powdered polyimide resin was applied to one surface of the panel. The resin used was Kerimid resin type 601 available from Rhone-Poulenc, Inc., Chemical Division, Monmouth Junction, N.J. 08852. The resin was applied by using two standard paint rollers, attached such that one roller led to the second roller (in tandem). This type of applicator was used in order to precisely control the amount of resin to be applied. The content of resin applied ranged from 25 percent to 30 percent by weight.

The coated panel was then placed onto the conveyor belt of the oven unit and was passed through the oven at a rate of approximately one half to five feet per second. During oven processing of the panel, the temperature of the oven was maintained at between 100° C. and 150° C.

Following the oven processing step, which formed a semi-continuous glassy-like resin coating on the upper surface of the cloth, the coated panel was cut into 4 $\frac{1}{2}$  inches by 4 $\frac{1}{2}$  inches swatches. The fusion of the resin onto the fabric greatly improved the handling characteristics of the material and no spalling or flaking of resin was observed. This minimized inhalation hazards and made precise control of resin content possible. The cut swatches were then superimposed upon one another

in 0° to 90° layup, alternating coated and uncoated surfaces, since the material had resin on only one side.

Following lay-up, the preform was warm pressed to stops, which controlled thickness and fiber volume, at 225° F. for 30 minutes. After this, temperature was increased to 350° F. and held for 60 minutes. After the 350° F. cycle, the power was turned off, water cooling to the platens was turned on, and the part was allowed overnight to cool. The 4 $\frac{1}{4}$  inch by 4 $\frac{1}{4}$  inch by 0.550 composite was removed from the press. The shaped substrate thus formed was well bonded, i.e., the edges could not be separated by gentle thumb abrasion.

Following the shaped substrate fabrication, the substrate was placed into a chemical vapor deposition apparatus and was controllably infiltrated with pyrolytic carbon. Fiber volume of the finished part was held to within 20 percent of that of the preform, i.e., the organic binder held through thermal processing to achieve the inorganic carbon binding. Calculated resin char content in the final discs was 2 to 3 percent by weight. This great reduction in content from 25 to 30 percent starting content is due to the poor char yield (by design) and the fact that the primary bond is the pyrolytic carbon which is added subsequently.

#### EXAMPLE NO. 2

Rayon precursor 8 H/S fabric was processed in the same manner as the fabric described in Example No. 1. The coated rayon fabric exhibited excellent handling characteristics and could be cut quite easily. No spalling or flaking of the resin was observed during cutting.

#### EXAMPLE NO. 3

Panels of fully carbonized 8 Harness Satin (8 H/S) PAN fabric were cut into several 11.30 inch circular discs. Binder material in the form of a furane resin distributed by Fiberite, Inc. was diluted with isopropyl alcohol in a 3:1 ratio for application. The resin solvent mixture was then sprayed on one side of each disc using a standard type of spray gun. The discs were then air dried for 24 hours at ambient temperature. Next, the discs were reweighed and the extent of resin pick-up was determined. Nominal resin pick-ups by weight were found to be about 3.0 percent. This was increased to 10 percent by subsequent spray coatings.

Each coated disc was then cut into 45° segments having an outside diameter (OD) of 10.30 inches and an inside diameter (ID) of 3.84 inches. Segments were laid up on a large plate having a graphite center "spud" or post. Each subsequent layer (8 segment group) was 50 rotationally offset from the preceding layer.

The fabric assemblies or basic substrates were compressed using a 350 ton press provided with heated platens. Press platens were heated to 250° F., materials were inserted, and the press was closed. Platen temperatures were maintained at 250° F. until thermocouples disposed within the material indicated that a temperature of 250° F. had been reached within the substrate. Platen temperatures and the material temperature were then increased to 350° F. The material was held at 350° F. for 10 minutes and then cooled down over a period of one hour. Pressure on the parts was maintained at approximately 350 pounds per square inch (PSI) throughout the pressing cycle.

Rigidized preforms, or shaped substrates, were obtained. Fiber volumes associated with the PAN 8 H/S preforms were about 27.9 percent. Preform density levels were about 0.531 grams per cubic centimeter

(gm/cc). The amount of binding material contained in the shaped substrates ranged from about 10 weight percent to about 15 weight percent. Preform quality as determined both visually and by x-ray analysis was excellent. No delaminating or microcracking was observed.

The shaped substrate was then subjected to a CVD processing cycle where resin carbonization, additional fiber bonding, and preform densification were achieved simultaneously. Dimensional changes, OD and ID, were minimal (0.04 to 2.2 percent). Major thickness expansion did, however, occur. Corresponding fiber volume (reduction) was about 20.4 percent. Calculated resin char content by weight was about 1 to 2 percent after final CVD. Densified preform (composite) quality was excellent. No delamination or macrocracking was observed. Thus, the major changes in thickness and fiber volumes observed were successfully accommodated without structural degradation. A high degree of substrate open porosity was maintained and uniformly increased.

Additionally CVD processing resulted in a final product, carbon/carbon composite with a density of about 1.75 gms/cc. Final composite quality was excellent (structurally sound) and mechanical property levels were highly acceptable.

#### EXAMPLE NO. 4

Full graphitized (rayon precursor) graphite 8 H/S fabric was processed in example the same manner as were the PAN fabrics described in Example No. 1. Resin content, however, was about 35 percent by weight and the discs were exposed to oven temperature for a total time of about 4 to 5 seconds.

After coating, the rayon discs were substantially more rigid and exhibited excellent handling characteristics. The assembly of the discs onto the plates of the fixture was accomplished with no spalling or flaking of the resin being observed.

Fiber volume of the finished article was measured and was found to be within 20 percent of that of the shaped substrate.

Calculated resin char content was about 3.5 percent by weight in the final disc after infiltration by CVD.

#### EXAMPLE NO. 5

A compressible non-woven carbonized pitch felt (mat) fibrous material was processed in the exact manner as was the PAN fabric described in Example No. 3.

A furane resin distributed by Fiberite, Inc. was used and the resin content was limited to about 15 percent by weight and the discs were exposed to oven temperature for about 2 hours. Calculated resin char content was about 2 percent by weight in the final disc after infiltration by CVD.

#### EXAMPLE NO. 6

A PAN woven fabric was processed in the exact manner as the rayon fabric described in Example No. 4 except that a furane resin distributed by Fiberite, Inc. was used and the resin content was limited to about 20 percent by weight. Calculated resin char content in the final disc was, again, about 2 percent.

#### EXAMPLE NO. 7

Carbonized PAN chopped fibers were suction deposited on a screen from a solution containing a liquid starch (polysaccharide) binder prepared by Purex

11

Corp., Carson, Calif. Enough residue from the initial solution was left on the fibers so that when they were dried in a press under 2 to 5 tons pressure in discs twelve inches in diameter, the starch binder set and held the discs in debulked condition through CVD bonding. Final product calculated starch char carbon content was only 1 to 2 percent by weight.

## EXAMPLE NO. 8

A compressible non-woven carbonized pitch felt (mat) fibrous material was processed in the exact manner as was the PAN fabric described in Example No. 3.

A phenolic resin of a common type which is readily commercially available was used and the resin content was limited to about 15 percent by weight and the discs were exposed to oven temperature for about 2 hours. Calculated resin char content was about 2 percent by weight in the final disc after infiltration by CVD.

## EXAMPLE NO. 9

A compressible non-woven carbonized pitch felt (mat) fibrous material was processed in the exact manner as was the PAN fabric described in Example No. 3.

An epoxy novalac of a common type which is readily commercially available was used and the resin content was limited to about 15 percent by weight and the discs were exposed to oven temperature for about 2 hours. Calculated resin char content was about 2 percent by weight in the final disc after infiltration by CVD.

## EXAMPLE NO. 10

A compressible non-woven carbonized pitch felt (mat) fibrous material was processed in the exact manner as was the PAN fabric described in Example No. 3.

An epoxy novalac/polyimide mix was used and the resin content was limited to about 15 percent by weight and the discs were exposed to oven temperature for about 2 hours. Calculated resin char content was about 2 percent by weight in the final disc after infiltration by CVD.

Having now described the invention in detail in accordance with the requirements of the patent statutes, those skilled in this art will have no difficulty in making changes and modifications in the individual parts or their relative assembly in order to meet specific requirements or conditions. Such changes and modifications may be made without departing from the scope and spirit of the invention, as set forth in the following claims.

I claim:

1. A method of making a carbon composite product comprising the steps of:

- (a) selectively depositing a precisely determined, limited amount of a carbonaceous binder material onto a compressible fibrous material;
- (b) subjecting said material and binder material to an elevated temperature of about 110° C. for a time period of about 3 seconds to thermally fuse said binder material to the fibers of said material intermittently of the length of said fibers to form a coated material;
- (c) cutting said coated material into swatches of a predetermined size and shape;
- (d) constructing said swatches into a basic substrate having a volume greater than the volume of the final product;
- (e) subjecting said basic substrate to controllable external pressures of up to 5000 psi at a predeter-

12

mined elevated temperature necessary to thermally fuse said binder material to the fibers of said material to compress said basic substrate into a shaped substrate having a known volume and a shape substantially corresponding to the shape desired of the final product, whereby said fibers are bonded together at a multiplicity of spaced apart bonding sites being free to move in response to stresses imparted to said shaped substrate, said shaped substrate thus formed being rigid, easily handleable and transportable and being capable of further processing without the need for holding fixtures or other means of external support;

- (f) subjecting said shaped substrate in a free standing configuration to elevated temperatures while controllably depositing pyrolytic material interstitially thereof, whereby said carbonaceous binder material is carbonized and said fibers are permanently bonded together by said pyrolytic material; and
- (g) continuing said interstitial deposition of pyrolytic material until the desired final product density is achieved.

2. A method of making a product as defined in claim 1 in which said compressible fibrous material is selected from the group consisting of pitch, rayon and polyacrylonitrile fibers and in which the amount of resin char bonding material contained in said final product is between approximately 1 weight percent and approximately 5 weight percent.

3. A method of making a product as defined in claim 1 including the interim step of heat treating said shaped substrate to a temperature of approximately 1600° C. to fully carbonize, purify and provide further dimensional stability to said shaped substrate prior to depositing pyrolytic material interstitially thereof.

4. A method of making a carbon composite product comprising the steps of:

- (a) selecting a compressible fibrous material made up of fibers selected from the group consisting of pitch, rayon and polyacrylonitrile;
- (b) cutting said selected material into swatches of a predetermined size and shape;
- (c) selectively depositing a precisely determined, limited amount of a carbonaceous binder material onto the fibers of each of said swatches;
- (d) subjecting said swatches and binder material to an elevated temperature of about 100° C. and about 150° C. for a time period of about 2 to 5 seconds to thermally fuse said binder material to the fibers of said swatches intermittently of the length of said fibers to form coated swatches;
- (e) cutting said coated swatches into segments of a predetermined size and shape;
- (f) constructing said swatches into a basic substrate having a volume greater than the volume of the final product;
- (g) subjecting said basic substrate to controllable external pressures of up to 5000 psi at a predetermined elevated temperature necessary to thermally fuse said binder material to the fibers of said material to compress said basic substrate into a shaped substrate having a known volume and a shape substantially corresponding to the shape desired of the final product, whereby said fibers are bonded together at a multiplicity of spaced apart bonding sites, said fiber portions disposed intermediate said bonding sites being free to move in response to stresses imparted to said shaped substrate, said

13

shaped substrate thus formed being rigid, easily handleable and transportable and being capable of further processing without the need for holding fixtures or other means of external support;

- (h) subjecting said shaped substrate in a free standing configuration to elevated temperatures while controllably depositing pyrolytic material interstitially thereof, whereby said carbonaceous binder material is carbonized and said fibers are permanently bonded together by said pyrolytic material; and
- (i) continuing said interstitial deposition of pyrolytic material until the desired final product density is achieved.

5. A method of making a carbon composite product as defined in claim 4 in which the amount of binder deposited on each said swatch is between about 34 and 38 percent by weight and in which the binder is intermittently deposited on the fibers so that the portions of

14

the fibers remained uncoated and free to move to accommodate stresses set up in the material.

6. A method of making a carbon composite product as defined in claim 4 in which the binder material is a phenolic resin.

7. A method of making a carbon composite product as defined in claim 4 in which the binder material is a furane resin.

8. A method making a carbon composite product as defined in claim 4 in which the binder material is a polyimide resin.

9. A method of making a carbon composite product as defined in claim 4 in which the binder material is a polysaccharide.

10. A method of making a carbon composite product as defined in claim 4 in which the binder material is an epoxy resin.

\* \* \* \* \*

20

25

30

35

40

45

50

55

60

65

# United States Patent [19]

Ichikawa et al.

[11] Patent Number: 5,037,699

[45] Date of Patent: Aug. 6, 1991

[54] HEAT-RESISTANT,  
CORROSION-RESISTANT INORGANIC  
COMPOSITE BODIES AND PROCESS FOR  
PREPARING THE SAME

[75] Inventors: Hiroshi Ichikawa; Shiro Mitsuno,  
both of Yokohama, Japan

[73] Assignee: Nippon Carbon Co., Ltd., Tokyo,  
Japan

[21] Appl. No.: 506,426

[22] Filed: Apr. 9, 1990

[30] Foreign Application Priority Data

Apr. 14, 1989 [JP] Japan ..... 1-93202

[51] Int. Cl.<sup>3</sup> ..... B32B 9/04

[52] U.S. Cl. ..... 428/408; 428/447

[58] Field of Search ..... 428/688, 701, 702, 408,  
428/447; 427/113, 115, 126.1, 294, 226, 255.1,  
255.3, 255.4

[56] References Cited

U.S. PATENT DOCUMENTS

4,418,097 11/1983 Misra ..... 427/397.7  
4,454,177 6/1984 Feist ..... 427/294  
4,753,855 6/1988 Haluska et al. ..... 428/688

Primary Examiner—Merrell C. Cashion, Jr.

Assistant Examiner—D. S. Nakarani

Attorney, Agent, or Firm—Bucknam and Archer

[57] ABSTRACT

A heat-resistant, corrosion-resistant inorganic composite body prepared by impregnating a heat-resistant inorganic compound body with at least one member selected from organosilicon compounds, metal alcohohlates and organosilicon compound-metal alcohohlate copolymers and then heat treating the thus impregnated body; and a process for preparing said heat-resistant, corrosion-resistant inorganic composite body.

4 Claims, No Drawings

# HEAT-RESISTANT, CORROSION-RESISTANT INORGANIC COMPOSITE BODIES AND PROCESS FOR PREPARING THE SAME

## **BACKGROUND OF THE INVENTION**

## 1. Field of the Invention

This invention relates to heat-resistant, corrosion-resistant inorganic composite bodies and a process for the preparation thereof and more particularly it relates to such inorganic composite bodies which may suitably be used as various articles under high-temperature and highly oxidizing conditions and are superior in various properties such as oxidation wear-resistance and heat-resistant strength, said various articles including pipes for blowing a gas therethrough into a molten metal, an article (such as a crucible for melting a metal therein) contacting with a molten metal, and electrodes for use in making electric furnace steel. The terms "oxidation-wear resistance" and "heat-resistant strength" are intended to mean "wear resistance under oxidizing conditions" and "strength under high temperature conditions" respectively.

## 2. Prior Art

Heat-resistant, corrosion-resistant inorganic composite bodies, such as an article contacting with a molten metal, which are used under high-temperature and highly oxidizing conditions, include heat-resistant inorganic compound bodies, such as artificial graphite bodies and C/C composites, which are composed mainly of carbon and/or graphite, and said bodies impregnated with a phosphoric acid compound such as phosphoric acid and salts thereof or coated with silicon dioxide ( $\text{SiO}_2$ ) or a metal oxide, such as alumina ( $\text{Al}_2\text{O}_3$ ), by plasma irradiation or the like.

However, the above-mentioned heat-resistant inorganic compound bodies composed mainly of carbon and/or graphite are not fully satisfactory in oxidation wear-resistance and heat-resistant strength and are difficult to use stably for a long period of time as an article contacting with a molten metal. Said heat-resistant inorganic compound bodies will be somewhat improved in oxidation wear-resistance by impregnating with a phosphoric acid compound or coating with a metal oxide, whereby heat-resistant and corrosion-resistant inorganic composite bodies having fully satisfactory properties cannot be obtained.

## SUMMARY OF THE INVENTION

In view of the above disadvantages, an object of this invention is to provide a new heat-resistant, corrosion-resistant inorganic composite body which is excellent in various properties such as oxidation wear-resistance and heat-resistant strength and may be used stably for a long period of time as an article contacting with a molten metal.

Another object of this invention is to provide a process for preparing said new heat-resistant, corrosion-resistant inorganic composite body.

In attempts to achieve these objects, the present inventors made intensive studies and found that a heat-resistant inorganic compound body is impregnated with at least one compound selected from the group consisting of specific organosilicon compounds, specific metal alcohohlates and specific organosilicon compound-metal alcohohlate copolymers, and then further heat treated thereby to obtain a new heat-resistant, corrosion-resistant inorganic composite body which is excellent in

properties such as oxidation-wear resistance and heat-resistant strength. This invention is based on the above finding or discovery.

The new heat-resistant, corrosion-resistant inorganic composite body of this invention may be obtained by:

(I) impregnating a heat-resistant inorganic compound body with at least one member of compound selected from the group consisting of

(A) organosilicon compounds having a polycarbosilane skeleton as the main skeleton and being preferably straight-chain ones, represented by the general formula (1)



20 wherein R<sub>1</sub> and R<sub>2</sub> are each an alkyl group preferably having 1-6, more preferably having 1-3 carbon atoms, phenyl group or hydrogen atom and may be identical with, or different from, each other; and m is an integer of 5-50.

(B) metal alcoholates represented by the general formula (2)



30 wherein  $M_1$  is zirconium, aluminium, silicon or titanium,  $R_3$  is an alkyl group preferably having 1-6, more preferably having 1-3 carbon atoms, phenyl group or hydrogen atom, and  $x$  is 3 or 4, and

(C) organosilicon compound-metal alcoholate copolymers having a modified polycarbosilane skeleton as the main skeleton, represented by the general formula (3)



wherein  $M_2$  is zirconium, aluminium, silicon or titanium;  $R_4$ ,  $R_5$  and  $R_6$  are each an alkyl group preferably having 1-6, more preferably having 1-3 carbon atoms, phenyl group or hydrogen atom and may be identical with, or different from, one another;  $y$  is 2 or 3; and  $n$  is an integer of 5-50, and then

50 (II) heat treating said heat-resistant inorganic compound body so impregnated.

This invention will be explained hereunder in more detail.

(A), (B) and (C) as explained above.

Among these compounds (A), (B) and (C), the compound (C), which is an organosilicon compound-metal alcoholate copolymer, may be obtained by subjecting at least one kind of the organosilicon compounds (A) and at least one kind of the metal alcoholates (B) to polycondensing reaction at an elevated temperature in an inert atmosphere. There are no particular limitations set on the combination of the compounds (A) and (B) which are used as starting compounds, and these compounds (A) and (B) may suitably be selected depending on a desired copolymer (C) to be obtained. The mixing ratio

between the organosilicon compound (A) and the metal alcoholate (B) is preferably 0.1-8.0 and particularly preferably 0.25-4.0 since the use of the latter mixing ratio will tend to result in the production of a copolymer having more improved oxidation resistance and more improved corrosion resistance to a molten metal. The conditions, such as the inert atmosphere, temperature and reaction time, under which said starting compounds (A) and (B) are polycondensed, are so suitably selected that the polycondensing reaction proceeds efficiently thereby to produce a copolymer (C), the end product, satisfactorily; the atmosphere, temperature and time are, for example, a nitrogen atmosphere, 100°-500° C. and 0.1-50 hours, respectively.

The heat-resistant inorganic compound body used in this invention may be a conventionally used one only if the conventionally used one is a porous heat-resistant inorganic compound body. A heat-resistant inorganic compound body composed mainly of carbon and/or graphite is preferable, and an artificial graphite body or a C/C composite is particularly preferable. The term "body" used herein is intended to mean a body which has been formed in compliance with the form of an article (end product) of this invention to be obtained.

There will be shown hereunder a general process for preparing the heat-resistant inorganic compound body used in this invention.

The starting material used in preparing the above inorganic compound body is at least one member selected from coke powder, carbon powder and graphite powder each of which may, if necessary, be incorporated with SiC powder or alumina powder, or is at least one member selected from carbon fibers, graphite fibers, SiC fibers and alumina fibers. Said starting material is incorporated with as a binder a resin, such as a phenol resin or furan resin, or pitch which will be carbonized by firing, molded into a desired shape and then fired at 700°-1200° C. for carbonization. The carbonaceous molding so obtained may be used as a heat-resistant inorganic compound body in this invention. In addition, a molding obtained by graphitizing at 2000°-3000° C. the above carbonaceous molding is preferable for use in this invention, and, further, a molding obtained by repeating plural times such impregnation with the resin or pitch, such carbonization and such graphitization as above is particularly preferable.

As previously mentioned, the heat-resistant and corrosion-resistant inorganic composite bodies of this invention are characterized in that they are obtained by impregnating said starting heat-resistant inorganic compound body with at least one member selected from the group consisting of said compounds (A), (B) and (C) and then heat treating the thus impregnated body.

There will be explained hereunder a preferable process for preparing the heat-resistant and corrosion-resistant inorganic composite bodies of this invention.

First of all, the starting heat-resistant inorganic compound body is impregnated with at least one member selected from the compounds (A), (B) and (C). As to this impregnation, the starting inorganic compound body is placed in a vessel such as an autoclave, the vessel is evacuated to an extent that its inner pressure is decreased to 10 Torr or lower, a suitable amount of the impregnant (A), (B) and/or (C) is injected into the vessel and an inert gas such as nitrogen is then introduced thereto, after which the pressure of the inert gas in the vessel is raised to 1-20 kg/cm<sup>2</sup> and then maintained at not higher than 100° C. for 1-100 hours to complete the

impregnation. In a case where it is difficult to impregnate the starting inorganic compound body with the impregnant, the impregnant may be incorporated with an organic solvent such as xylene in an amount of not higher than 50% by weight of the impregnant for facilitating the impregnation.

Then, the starting body so impregnated is heat treated to obtain a heat-resistant, corrosion-resistant inorganic composite body of this invention. As to this 10 heat treatment, it is preferable that said starting body so impregnated is heated at a temperature-raising rate of 5°-30° C./hr to 100°-700° C. in an oxidizing atmosphere such as air and then further heated at a temperature-raising rate of 100°-250° C./hr to 150°-2500° C. in a non-15 oxidizing atmosphere such as nitrogen.

In cases where heat treatment is effected under operational conditions other than the above ones used in this invention, no desired heat-resistant, corrosion-resistant inorganic composite bodies undesirably tend to be obtained.

There will be obtained desired heat-resistant, corrosion-resistant inorganic composite bodies of this invention even by carrying out the above impregnation and heat treatment one time each. In addition, there will 20 preferably be obtained further desired inorganic composite bodies of this invention by carrying out the above impregnation and heat treatment several times each thereby enabling the impregnant to be impregnated more highly densely into the pores of the starting inorganic compound body to be impregnated.

The heat-resistant, corrosion-resistant inorganic composite bodies of this invention so obtained have a widely inhibited oxidation-wear rate at about 600° C. and enhanced flexural strength as compared with conventional ones such as the starting heat-resistant inorganic compound body and this body impregnated with a phosphoric acid compound. Further, the heat-resistant, corrosion-resistant inorganic composite bodies of this invention obtained from a starting heat-resistant inorganic compound body having electrical conductivity such as a graphite body, are more excellent in oxidation-wear resistance and heat-resistant strength than conventional electrodes for electric furnace steel and are useful as electrodes for electric furnace steel.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention will be better understood by the following examples in comparison with the following comparative Examples.

#### EXAMPLES 1-8

The compounds (impregnants) to be impregnated into starting heat-resistant inorganic compound bodies indicated in Table 1, which impregnants are also indicated in Table 1, were mixed with xylene in the respective ratios indicated in Table 1.

The copolymers (C1-C6) used in Examples 3-8 were prepared by mixing together the starting compounds indicated in Table 2 in the respective ratios indicated in the same Table and then polycondensing the respective mixtures in a nitrogen atmosphere under reaction conditions indicated in the above Table.

The artificial graphite bodies indicated in Table 1, which are used as starting heat-resistant inorganic compound bodies, were previously subjected to supersonic washing in acetone for 10 minutes and then dried at 250° C. in air for one hour.

The artificial graphite bodies so washed and dried were each placed in an autoclave which was then reduced to  $10^{-1}$  Torr in inner pressure. Thereafter, the mixtures of said compounds (impregnants) and xylene were each poured into the evacuated autoclave, nitrogen gas was blown thereto and said bodies were impregnated respectively with said compounds (impregnants) under the respective impregnating conditions shown in Table 1.

The thus impregnated artificial graphite bodies were heat treated in air under the respective conditions shown in Table 1 and then further heat treated in a nitrogen atmosphere under the respective conditions indicated in the same Table.

The above impregnation and heat treatment were each repeated plural times to obtain heat-resistant, corrosion-resistant inorganic composite bodies respectively of Examples 1-8.

The heat-resistant, corrosion-resistant inorganic composite bodies of Examples 1-8 were measured for their flexural strength by autograph. They were maintained at  $600^{\circ}\text{C}$ . in air for 50 hours to measure their oxidation-wear rate. The results are as shown in Table 3.

Further, the heat-resistant, corrosion-resistant inorganic composite bodies of Examples 4-8 were each made into a tube for blowing a gas therethrough which was fitted in a furnace for highly purifying aluminium

alloys. The gas was repeatedly blown through the tube into a molten aluminium alloy heated at  $720^{\circ}-740^{\circ}\text{C}$ . (one time every 5 minutes); it was measured in this manner how many times the gas could be repeatedly blown into the molten alloy before the tube became useless by its oxidation wear and decrease in strength due to the molten alloy. The results are also as shown in Table 3.

#### COMPARATIVE EXAMPLES 1-2

In comparative Example 1, the same washed artificial graphite body as used in Examples 1-8 was used without such impregnation and heat treatment as mentioned above to measure its flexural strength and oxidation-wear rate in the same manner as in Examples 1-8. In comparative Example 2, the procedure of comparative Example 1 was followed that the same washed artificial graphite body was impregnated with phosphoric acid in the same manner as in Examples 1-8 under the impregnation treating conditions indicated in Table 1. The results are as indicated in Table 3.

In addition, the artificial graphite body of Comparative Example 1 was used as a gas blowing tube of a furnace for highly purifying aluminium alloys to measure in the same manner as in Examples 4-8 how many times the gas could be repeatedly blown through the tube. The result is also as shown in Table 3.

TABLE 1

Example Comp. Ex.	Heat-resistant inorganic compound body		Compound (Impregnant)	Conc. of xylene (wt. %)	Impregnation treating conditions		
	Pressure Kg/cm <sup>2</sup>	Temp. °C.			Time hr		
Example 1	Artificial graphite body 1* <sup>1</sup>	Polycarbosilane (A1)* <sup>4</sup>	30	5	20	24	
Example 2	Artificial graphite body 1* <sup>1</sup>	Tetrabutoxyzirconium (B1)* <sup>5</sup>	12	10	20	15	
Example 3	Artificial graphite body 1* <sup>1</sup>	Polycarbosilane- tetrabutoxyzirconium copolymer (C1)	20	10	20	15	
Example 4	Artificial graphite body 2* <sup>2</sup>	Polycarbosilane- tetrabutoxytitanium copolymer (C2)	25	10	20	15	
Example 5	Artificial graphite body 2* <sup>2</sup>	Polycarbosilane- tetrabutoxytitanium copolymer (C3)	25	10	20	15	
Example 6	Artificial graphite body 2* <sup>2</sup>	Polycarbosilane- tetrabutoxytitanium copolymer (C4)	25	10	20	15	
Example 7	Artificial graphite body 2* <sup>2</sup>	Polycarbosilane- tetrabutoxytitanium copolymer (C5)	25	10	20	15	
Example 8	Artificial graphite body 2* <sup>2</sup>	Polycarbosilane- tetrabutoxytitanium copolymer (C6)	25	10	20	15	
Comp. Ex. 1	Artificial graphite body 1,2* <sup>3</sup>	—	—	—	—	—	
Comp. Ex. 2	Artificial graphite body 1* <sup>1</sup>	Phosphoric acid	—	5	20	15	

Example Comp. Ex.	Heat treating conditions				Times of impregnation and of heat treatment	
	In air		In nitrogen atmosphere			
	Temp.-raising rate °C./hr	Max. temp. °C.	Temp.-raising rate °C./hr	Max. temp. °C.		
Example 1	10	250	200	1000	2	
Example 2	10	250	200	1000	2	
Example 3	20	350	180	1150	3	
Example 4	20	350	180	1150	3	
Example 5	20	350	180	1150	3	
Example 6	20	350	180	1150	3	
Example 7	20	350	180	1150	3	
Example 8	20	350	180	1150	3	
Comp. Ex. 1	—	—	—	—	—	

TABLE 1-continued

Comp. Ex. 2

- \*<sup>1</sup>Produced by Nippon Carbon Co., Ltd.; Tradename, EG-38; Bulk specific gravity, 1.70; Size, 20 mmφ × 300 mm length.  
 \*<sup>2</sup>Produced by Nippon Carbon Co., Ltd.; Tradename, EG-38; Bulk specific gravity, 1.70; Size, 120 mmφ × 400 mm length.  
 \*<sup>3</sup>Artificial graphite body 1 (\*<sup>1</sup>) was used to measure flexural strength and oxidation-wear rate, and body 2(\*<sup>2</sup>) used to measure performance as gas blowing tube.  
 \*<sup>4</sup>Average molecular weight, about 2000; Basic skeleton, —(SiHCH<sub>2</sub>CH<sub>2</sub>)—.  
 \*<sup>5</sup>Structural formula, Zr (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>.

TABLE 2

Example	Compound (C) (Impregnant)	Starting compounds for preparing Compound (C)		Mixing ratio (A/B) Wt. ratio	Polycondensing reaction conditions	
		Organosilicon compound (A)	Metal alcoholate (B)		Temp. (°C.)	Time (hr)
Example 3	Polycarbosilane-tetrabutoxyzirconium copolymer (C1)	Polycarbosilane (A1)* <sup>1</sup>	Tetrabutoxyzirconium (B1)* <sup>3</sup>	4/1	200	1.0
Example 4	Polycarbosilane-tetrabutoxytitanium copolymer (C2)	Polycarbosilane (A2)* <sup>2</sup>	Tetrabutoxytitanium (B2)* <sup>4</sup>	1/10	250	1.5
Example 5	Polycarbosilane-tetrabutoxytitanium copolymer (C3)	Polycarbosilane (A2)* <sup>2</sup>	Tetrabutoxytitanium (B2)* <sup>4</sup>	1/4	250	1.5
Example 6	Polycarbosilane-tetrabutoxytitanium copolymer (C4)	Polycarbosilane (A2)* <sup>2</sup>	Tetrabutoxytitanium (B2)* <sup>4</sup>	1/1	250	1.5
Example 7	Polycarbosilane-tetrabutoxytitanium copolymer (C5)	Polycarbosilane (A2)* <sup>2</sup>	Tetrabutoxytitanium (B2)* <sup>4</sup>	4/1	250	1.5
Example 8	Polycarbosilane-tetrabutoxytitanium copolymer (C6)	Polycarbosilane (A2)* <sup>2</sup>	Tetrabutoxytitanium (B2)* <sup>4</sup>	8/1	250	1.5

<sup>1</sup>Average molecular weight, about 2000; Basic skeleton, —(SiHCH<sub>2</sub>CH<sub>2</sub>)—.<sup>2</sup>Average molecular weight, about 2500; Basic skeleton, —(SiHCH<sub>2</sub>CH<sub>2</sub>)—.<sup>3</sup>Structural formula, Zr (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>.<sup>4</sup>Structural formula, Ti (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>.

TABLE 3

	Flexural strength [kg/cm <sup>2</sup> ]	Oxidation- wear rate [wt. %]	performance as gas blowing pipe (Times of repeated use)
Example 1	530	11.3	—
Example 2	540	10.9	—
Example 3	560	9.5	—
Example 4	550	12.5	338
Example 5	560	9.1	399
Example 6	567	9.1	406
Example 7	563	9.2	392
Example 8	544	12.8	343
Comp. Ex. 1	400	30.9	60
Comp. Ex. 2	400	25.2	—

Note: Comp. Ex. = Comparative Example

## EXAMPLE 9 AND COMPARATIVE EXAMPLE 3

A plain-weave cloth consisting of carbon filaments 6000 f was impregnated with a phenol resin in an amount of 40% by weight thereof to prepare a prepeg. Twenty of prepegs so prepared were laminated with one another, molded and cured at 150° C., carbonized at 800° C. and then graphitized at 2000° C. to obtain a plate-like molding having a size of 5 × 30 × 300 mm. The thus obtained plate-like molding was impregnated with pitch, carbonizing at 800° C. the pitch-impregnated molding, repeating these impregnation and carbonization two more times, and further heating to 2000° C. the thus carbonized molding to again graphitize it thereby obtaining a C/C composite. The composite so obtained had a bulk specific gravity of 1.60.

The C/C composite so obtained was placed in an autoclave which was then reduced in pressure to 10<sup>-1</sup> Torr. Thereafter, tetrabutoxytitanium (B2) was poured, without mixing with an organic solvent, into the autoclave, nitrogen gas was introduced into the autoclave to pressurize the inside thereof to 10 kg/cm<sup>2</sup>, and the auto-

clave was then maintained at this pressure and 40° C. for 15 hours thereby to impregnate the C/C composite with the tetrabutoxytitanium (B2).

Subsequently, the C/C composite so impregnated was heated in air at a temperature-raising rate of 10° C./hr to 250° C. and then further heated at a temperature-raising rate of 200° C./hr to 1000° C. in a nitrogen atmosphere thereby to obtain a heat-resistant, corrosion resistant inorganic composite body of Example 9.

The thus obtained heat-resistant, corrosion-resistant inorganic composite body (Example 9) and the above C/C composite prepared without impregnation and heat treatment (Comparative Example 3) were each measured for flexural strength and oxidation-wear rate in the same manner as in Examples 1-8 with the results being shown in Table 4.

TABLE 4

	Flexural strength (kg/mm <sup>2</sup> )	Oxidation-wear rate (wt. %)
Example 9	18	12.8
Comp. Ex. 3	16	55.2

## EXAMPLE 10 AND COMPARATIVE EXAMPLE 4

An artificial graphite electrode (produced by Nippon Carbon Co., Ltd. and having a bulk specific gravity of 1.71, a flexural strength of 145 kg/cm<sup>2</sup> and a size of 16 inchφx6 feet length) was charged in an autoclave which was then reduced in pressure to 5 Torr. Thereafter, a mixture of acetone with the same polycarbosilane-tetrabutoxyzirconium copolymer (C1) as used in Example 3 (said mixture containing 20 wt. % of acetone) was poured into the autoclave, nitrogen gas was introduced

thereinto to increase the pressure to 5 kg/cm<sup>2</sup>, and the autoclave so charged was then maintained at this pressure and 40° C. for 24 hours thereby to impregnate the artificial graphite electrode with the copolymer (C1).

The thus impregnated artificial graphite electrode was heated in air at a temperature-raising rate of 10° C./hr to 250° C. and further heated in a nitrogen atmosphere at a temperature-raising rate of 250° C./hr to 1000° C. thereby to obtain a heat-resistant, corrosion-resistant inorganic composite body of Example 10.

The thus obtained heat-resistant, corrosion-resistant inorganic composite body (Example 10) and an artificial graphite electrode (comparative Example 4) which was not subjected to such impregnation and heat treatment as above, were each continuously used as an electrode in a 30 t steel-making electric furnace for 10 days, during which electrode consumption (expressed in terms of "kg of electrode consumed/ton of good ingot produced") was measured. The results are as shown in Table 5.

TABLE 5

	Electrode consumption (kg/ton of good ingot)
Example 10	2.6
Comp. Ex. 4	2.8

As is apparent from Table 3, all the new heat-resistant and corrosion-resistant inorganic composite bodies obtained by impregnating an artificial graphite body with a specific organosilicon compound (Example 1), a specific metal alcoholate (Example 2) or a specific organosilicon compound-metal alcoholate copolymer (Examples 3-8) and then heat treating the thus impregnated artificial graphite body, as compared with an artificial graphite body (Comparative Example 1) which has conventionally been used as a heat-resistant and corrosion-resistant inorganic composite body or such a body (Comparative Example 2) impregnated with phosphoric acid, are very excellent in oxidation-wear resistance (the oxidation-wear of the new bodies being less than about  $\frac{1}{2}$  of that of the conventional one) and enhanced flexural strength (the flexural strength of the new bodies being at least 1.3 times that of the conventional one).

Further, the heat-resistant, corrosion-resistant inorganic composite bodies of Examples 4-8 were able to be used for a long period of time as gas blowing tubes for highly purifying aluminium alloys and could be repeatedly used, the time of repetition being at least 5 times that of conventional graphite gas blowing tubes (Comparative Example 1).

As is clear from Table 4, even a new heat-resistant, corrosion-resistant inorganic composite body (Example 9) prepared by impregnating a C/C composite, which was a kind of conventional heat-resistant, corrosion-resistant inorganic composite body, with a specific organosilicon compound-metal alcoholate copolymer and then heat treating the thus impregnated C/C composite, is remarkably improved in oxidation-wear resistance and flexural strength as compared with a C/C composite (Comparative Example 3) without having undergone such impregnation and heat treatment.

Furthermore, as is apparent from Table 5, a new artificial graphite electrode (Example 10) obtained by impregnating a conventional artificial graphite electrode with a specific organosilicon compound-metal alcoholate copolymer and then heat treating the thus impregnated electrode, exhibited excellent electrode

consumption as compared with a conventional artificial graphite electrode (Comparative Example 4) when these two electrodes were each used as such in an electric furnace for making steel.

## EFFECTS OF THE INVENTION

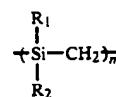
As is clear from the above description, this invention characterized by impregnating a heat-resistant inorganic compound body with at least one member selected from the group consisting of specific organosilicon compounds, specific metal alcoholates and specific organosilicon compound-metal alcoholate copolymers and then heat treating the thus impregnated body, makes it possible to obtain a new heat-resistant, corrosion-resistant inorganic composite body which is excellent in various properties such as oxidation-wear resistance and heat-resistant strength and is enabled to be used stably for a long period of time as articles contacting with a molten metal.

Particularly, in a case where an electrically conductive body, such as a graphite body, is used as the heat-resistant inorganic compound body in this invention, there will be obtained an electrode for making electric furnace steel, the electrode so obtained being improved in oxidation-wear resistance, etc. while maintaining its electrical conductivity and also being excellent in electrode consumption.

Thus the heat-resistant, corrosion-resistant inorganic composite bodies of this invention may suitably be used as an article contacting with a molten metal, an electrode for making electric furnace steel, or the like; and the process of this invention may suitably be used for producing the heat-resistant, corrosion-resistant inorganic composite body of this invention.

What is claimed is:

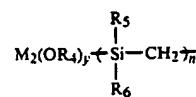
1. A heat-resistant, corrosion-resistant inorganic composite body obtained by:
  - (a) impregnating a heat-resistant inorganic compound body with at least one member selected from the group consisting of
    - (1) organosilicon compounds having a polycarbosilane skeleton as the main skeleton of formula



(1)

wherein R<sub>1</sub> and R<sub>2</sub> are each an alkyl group of 1-6 carbon atoms, phenyl or hydrogen and are identical or different from each other; and m is an integer of 5-50, and

(2) an organosilicon compound-metal alcoholate copolymer having a modified polycarbosilane skeleton as the main skeleton of formula (2)



(2)

wherein M<sub>2</sub> is zirconium, aluminium, silicon or titanium; R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> are each an alkyl group of 1-6 carbon atoms, phenyl or hydrogen and are identical or different from one another; y is 2 or 3; and n is an integer of 5-50,

11

- (b) heating the thus impregnated heat-resistant inorganic compound body to 100°-700° C. in an oxidizing atmosphere and then
  - (c) heating the thus heated inorganic compound body to 150°-2500° C. in a non-oxidizing atmosphere.
2. A heat-resistant, corrosion-resistant inorganic composite body according to claim 1, wherein said heat-resistant inorganic compound body consists of carbon.
3. A heat-resistant, corrosion-resistant inorganic com-

12

posite body according to claim 1, wherein said heat-resistant inorganic compound body consists of graphite.

- 4. A heat-resistant, corrosion-resistant inorganic composite body according to claim 1, wherein said heat-resistant inorganic compound body consists of carbon and graphite.

\* \* \* \* \*

10

15

20

25

30

35

40

45

50

55

60

65



US005397643A

**United States Patent [19]**

von Bonin et al.

[11] Patent Number: 5,397,643

[45] Date of Patent: Mar. 14, 1995

[54] **LIGHTWEIGHT SHAPED ARTICLES  
CONTAINING EXPANDABLE GRAPHITE,  
THEIR PRODUCTION AND THEIR USE**

[75] Inventors: Wulf von Bonin, Odenthal; Ulrich von Gizecki, Leverkusen, both of Germany

[73] Assignee: Bayer Aktiengesellschaft, Leverkusen, Germany

[21] Appl. No.: 33,445

[22] Filed: Mar. 18, 1993

**Related U.S. Application Data**

[63] Continuation of Ser. No. 678,100, Apr. 1, 1991, abandoned, which is a continuation-in-part of Ser. No. 504,360, Apr. 3, 1990, Pat. No. 5,053,148.

**[30] Foreign Application Priority Data**

Apr. 11, 1990 [DE] Germany ..... 40 11 697.2

[51] Int. Cl. 6 ..... C04B 35/52; C04B 14/32  
[52] U.S. Cl. ..... 428/408; 428/305.5;  
423/448; 521/54; 521/55; 523/179

[58] Field of Search ..... 428/305.5, 408;  
423/448; 521/54, 55; 523/179

**[56] References Cited****U.S. PATENT DOCUMENTS**

4,146,401	3/1979	Yamada et al. ....	106/56
4,432,408	2/1984	Caines ....	165/1
4,676,515	6/1987	Cobb ....	277/235 B
4,694,030	9/1987	Von Bonin et al. ....	523/179
4,723,783	2/1988	Belter et al. ....	277/235 B
4,892,783	1/1990	Brazel ....	428/408
4,973,516	11/1990	Yamaoka et al. ....	428/332
5,053,148	10/1991	von Bonin ....	252/8.05
5,094,780	3/1992	Von Bonin ....	428/408

**FOREIGN PATENT DOCUMENTS**

0059866	9/1982	European Pat. Off. .
0061636	10/1982	European Pat. Off. .
0164984	12/1985	European Pat. Off. .
3912552	10/1990	Germany .
2169273	7/1986	United Kingdom .

*Primary Examiner*—George F. Lesmes

*Assistant Examiner*—Blaine R. Copenheaver

*Attorney, Agent, or Firm*—William C. Gerstenzang

**[57] ABSTRACT**

Sandwich-like lightweight shaped articles consist of a core material containing expandable graphite expanded according to the mould and if appropriate a binder, and at least one covering layer of thermoplastic material.

1 Claim, No Drawings

**LIGHTWEIGHT SHAPED ARTICLES  
CONTAINING EXPANDABLE GRAPHITE, THEIR  
PRODUCTION AND THEIR USE**

This application is a continuation, of application Ser. No. 678,100, filed Apr. 4, 1991, now abandoned, which is a continuation-in-part of Ser. No. 07/504,360, filed Apr. 3, 1990, now U.S. Pat. No. 5,053,148, issued Oct. 1, 1991.

The present invention relates to sandwich-like lightweight shaped articles, the core material of which contains expanded expandable graphite, and a process for their production and their use.

Known sandwich-like lightweight shaped articles having a relatively high heat resistance contain as the core material, for example, foamed glass which has been joined to the covering layers by glueing. The disadvantage of these is that the heat resistance is not high enough for many purposes, and the production of specifically shaped lightweight articles is difficult.

Sandwich-like lightweight shaped articles have now been found, which are characterised in that their core material contains expandable graphite expanded according to the mould, and at least one covering layer consists of a thermoplastic material.

The core material of the lightweight shaped articles according to the invention can only consist of expanded expandable graphite, or it can also consist of mixtures which are obtained when non-expanded or only partly expanded expandable graphite is heated, together with binders and/or fillers, to temperatures at which the expandable graphite expands.

Possible expandable graphites are, for example, modified graphites which expand when heated to temperatures above 150° C. Such graphites are known and are commercially available. They can contain as blowing agents, for example, incorporated NO<sub>x</sub>; SO<sub>x</sub>; H<sub>2</sub>O; halogens or strong acids. NO<sub>x</sub> and SO<sub>x</sub> expandable graphites are preferred. Surprisingly, these aggressive blowing gases cause no trouble.

The expandable graphite can be employed, for example, as a flaky or flocked powder, as granules or in the form of pre-shaped pieces. Mixtures of expandable graphites of various forms and/or types are also possible. The expandable graphite can also already be partly expanded before it is employed.

Possible binders which can be employed, if appropriate, as a mixture with the expandable graphite to be expanded are, for example, thermoplastics, such as are described below as the material for the covering layers, as well as ortho-, meta-, pyro- and polyphosphates, phosphonates, borates and silicates which contain metal ions of metals of group 1 to 3 of the periodic table, ammonium or amines as the cationic components, and distillation residues and carbon powder. In the case of phosphates, polyphosphates, phosphonates, borates and silicates having a cationic component based on an amine, possible amines are, for example, ammonia, ethylenediamine, propylenediamine, polyalkylenepolyamines, alkanolamines, aniline, anilineformaldehyde condensates and melamine. The binders are preferably fusible.

Preferred phosphates, polyphosphates, phosphonates, borates and silicates are borax, ammonium phosphate, ammonium polyphosphate, ethylenediamine phosphate, melamine phosphate, melamine borate, melamine diphosphate, melamine polyphosphate, sodium

polyphosphate, zinc, calcium, aluminium and magnesium phosphonates and polyphosphates and alkali metal silicates, and in the case of the phosphonates in particular those which

- a) contain a phosphonate component of the formula (I)



in which

M represents aluminium, magnesium or calcium,

R represents an aliphatic radical having 1 to 6 C atoms or an aromatic radical having 6 to 10 C atoms,

R' represents hydrogen, an aliphatic radical having 1 to 6 C atoms or an aromatic radical having 6 to 10 C atoms and

x represents an integer corresponding to the valency of M, and 0.05 to 1 mol of an amine from the group comprising ammonia, ethylenediamine, polyethylenepolyamine, melamine, guanidine, urea, di-cyandiamide, anilineformaldehyde condensate, ethanolamine and dimethylaminopropylamine is present per equivalent of OR' groupings contained in the phosphonate component, or

- b) are a metal salt or metalloid salt of a phosphonic acid of the formula (II)



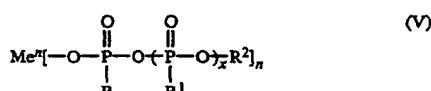
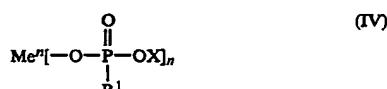
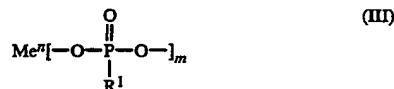
in which

R represents a straight-chain or branched C<sub>1</sub>- to C<sub>3</sub>-alkyl radical which is optionally substituted by halogen and/or OH and

R' represents hydrogen or a C<sub>1</sub>- to C<sub>3</sub>-alkyl radical, and

wherein the metal or metalloid is chosen from groups IIA, IIB, IIIA, IVA and VA of the periodic table, or

- c) correspond to one of the formulae (III) to (V)



in which, in each case,

Me represents a metal of main or sub-groups 2 or 3 of the periodic table,

n represents the valency of the metal Me,

m represents n/2,

R, R<sup>1</sup> and R<sup>2</sup> in each case independently of one another represent an organic radical having 1 to 18 C atoms,

X represents hydrogen, ammonium, alkylammonium or one equivalent of a metal and

x represents zero or an integer from 1 to 20.

Phosphates, especially neutral ethylenediamine phosphate and calcium and aluminium salts of polyphosphoric acids, are preferred binders. Where the binders can be distillation residues, examples of possible distillation residues are those such as are obtained during the preparation of aromatic isocyanates or during distillation of tar oil and petroleum. The latter are known by the name "bitumen" and are particularly advantageously employed as a mixture with phosphorus compounds, as is also, for example, mineral coal powder, or powders of other tar-rich coals or plant constituents.

It is also otherwise possible for mixtures of various binders to be employed.

The amount of binders, based on the total weight of the lightweight shaped articles, can be, for example, 0 to 85% by weight. It is preferably 10 to 35% by weight.

Surprisingly, binders containing phosphorus, in particular phosphates and phosphonates of the type mentioned, provide good protection for the core material of lightweight shaped articles according to the invention from oxidative attack by oxygen or air, in particular at temperatures above 500° C. The phosphates are particularly effective here, which is of importance for the lightweight shaped articles to be usable in the high temperature range. The electrical and thermal conductivity are retained here, which is of interest for specific intended uses, for example as heating elements.

If desired, the expandable graphite to be expanded can also be employed in combination with fillers which melt and/or do not melt under the particular production conditions. Such fillers can be, for example, in the form of fibres, beads, hollow beads or powders, and can consist, for example, of glass, quartz, carbon, chalk, asbestos, flyash, talc, calcined or slaked lime, hydrargillite, cement and/or kaolin. 0 to 75% by weight of fillers, for example, preferably 0 to 50% by weight, based on the total weight of the lightweight shaped articles, can be incorporated.

Possible thermoplastic materials of which at least one covering layer of the lightweight shaped articles according to the invention consists, preferably both if two covering layers are present, and which can also be used, if appropriate, as a binder additive to the expandable graphite to be expanded are, for example, organic and/or inorganic materials which soften or melt but do not decompose in an undesirable manner when heated to the production temperatures of lightweight shaped articles according to the invention. These can be very diverse types of materials, depending on what production temperatures are to be chosen. The thermoplastic materials preferably have a glass transition temperature above 150° C.

High production temperatures for lightweight shaped articles according to the invention, for example those above 900° C., can be applied if the thermoplastic materials employed are, for example, rock powders, in particular sintered or molten rock powders, slag, enamel frits, clay minerals, porcelain clays, other ceramic base materials, glasses or correspondingly high-melting metals or metal alloys, for example steel, copper, aluminium and/or silver.

Production temperatures below 1500° C., in particular those between 300° and 900° C., and metals, metal alloys, glasses, glass-ceramic compositions, organic-inorganic or organic-aromatic plastics which soften or melt in this range are preferably used for lightweight shaped articles according to the invention. Possible metals here are, for example, aluminium, lead, zinc and alloys containing these metals, possible glasses are, in particular, silicate glasses, such as soda-lime glasses, borosilicate glasses, aluminosilicate glasses and glasses with low expansion coefficients, possible organic-inorganic plastics are, for example, silicones, so-called ormosers (that is to say organically modified ceramic compositions) and phosphacenes, and possible organic-aromatic plastics are, for example, polyesters, polyethers, polyepoxides, polysulphides, polysulphones, polyimides, polyamides, polyanhidrides, polyketones, polycarbonates, polyhydantoins, polyoxazinediones, polyureas, polycarbodiimides, polyurethanes and LC polymers, each of which contains aromatic structures in the polymer chain, and mixtures thereof. Particularly preferred materials are silicate glasses, aluminium, aluminium alloys and polyphenylene sulphide.

Covering layers which soften only at high temperatures and which, if appropriate, are thermoplastically deformable at temperatures higher than the production temperature of the lightweight shaped articles can also be employed in the context of the present invention. Examples of such materials are steel, copper, silver, ceramic compositions and quartz.

In particular at low production temperatures for lightweight moldings according to the invention, e.g. at those below 300° C., polyolefins, for example polypropylene, polyethylene, polybutadiene, polystyrene, polyvinyl acetate, polyacrylate esters or mixtures thereof, are also suitable as thermoplastic materials. However, with these there is sometimes the risk that the polyolefins decompose in an undesirable manner before the expandable graphite employed has expanded sufficiently.

Thermoplastic materials for covering layers of the lightweight shaped articles according to the invention can be employed, for example, in the form of sheets, powders, granules or fibres or as textile sheet-like structures (mats, nonwovens). Sheet goods are preferred. If appropriate, the thermoplastic materials can contain additives, for example fillers, reinforcing fibres, stabilisers and/or dyestuffs.

Thermoplastic materials as a binder additive in the expandable graphite to be expanded are preferably employed in the form of powders, granules or synthetic fibres. In specific cases, the thermoplastic materials can also be used in sheet form here, if this is embedded in the expandable graphite layer.

Sandwich-like lightweight shaped articles according to the invention can be obtained by allowing expandable graphite which is capable of expansion and if appropriate contains a binder to expand at temperatures in the range from 200° to 2000° C. between two covering layers, at least one of which consists of a thermoplastic material.

The thermoplastic material and the material containing expandable graphite which is capable of expansion can be in a form as described above.

Preferred temperatures for the production are those from 300° to 900° C., in particular those from 300° to 600° C.

The following procedure is followed, for example, in a particular embodiment of the production process for lightweight shaped articles according to the invention:

A press with which sheets or other shapes can be produced is used. A flat spacer frame of steel is first laid in the press, the thermoplastic material for one covering layer is then introduced, followed by the material which contains expandable graphite and is capable of expansion, and then, if appropriate, the material for a second covering layer, which, if present, can consist of 10 thermoplastic material or another material. The spacer frame is then not yet filled up, but still leaves room for the expansion of the expandable graphite. For this, the press is heated up to the particular desired temperature, it being ensured that the press is secured in a pressure-resistant manner and is essentially closed but the expansion gases can still escape. The parts of the press which cover the spacer frame (for example steel sheets) are preferably provided with a mould release agent on their surface, for example with paper or talced aluminium foil for relatively low temperatures and with graphite, talc or aluminium oxide powder for relatively high temperatures. When the desired temperature has been reached 15 inside the mould, it is cooled and the resulting lightweight shaped article is then removed from the mould.

It is often advantageous to expand the expandable graphite with the exclusion of oxygen.

The thickness of the covering layer(s) and the density of the core material can be controlled by the amount of materials introduced into the press for these components. The covering layers consisting of thermoplastic material reproduce the surface shape of the press. Thus, for example, lightweight-shaped articles provided with embossing or a camber can also be obtained.

The core material of lightweight shaped articles according to the invention in general has a bulk density of less than 0.9 g/cm<sup>3</sup>. The bulk density is preferably in the range from 0.05 to 0.5 g/cm<sup>3</sup>. The core material is as a rule joined firmly to the material of the covering layers, especially if the latter has partly seeped into the core material during production of the lightweight shaped articles.

Lightweight mouldings according to the invention can be produced in a simple manner, for example as sheets, profiles or in other shapes to be achieved by 45 shell-like shaping. Cylindrical shapes in which the jacket consists of one of the thermoplastic materials described for covering layers and the core consists of expanded expandable graphite and if appropriate additives are also possible. Lightweight mouldings according to the invention withstand high temperatures, have a ductile, non-brittle core and can be further shaped and processed as thermoplastics. Lightweight mouldings according to the invention are in general superior to the known products both in respect of their heat stability and in respect of their low bulk density, especially if tough covering layers of lightweight organic polymers, for example those of polyphenylene sulphide or polyimides, or of aluminium are provided. The core material of lightweight mouldings according to the invention is in general thermally and electrically conductive and, in combination with insulating and metallic covering layers, opens up new possible uses.

The present invention also relates to the use of sandwich-like lightweight shaped articles, the core material of which contains expanded expandable graphite and in which at least one covering layer consists of a thermoplastic material, in the construction of apparatuses and

5 housings which can be used at high temperatures and for high-speed missiles, shock absorbers, rocket engines, turbines, combustion engines, exhaust gas ducts, antennae and thermal, electromagnetic and/or electrical shielding and insulating equipment.

In the following examples, parts and percentages relate to the weight, unless stated otherwise.

## EXAMPLES

### Example 1

Commercially available NO<sub>x</sub> expandable graphite which expands to more than 15 times its volume when heated to 600° C. under normal pressure was mixed with a binder which was prepared by reaction of 1 mol of aluminium hydroxide, 3 mol of dimethyl methylphosphonate and water in an autoclave at 180° C. and was obtained as a clear aqueous solution.

A steel mould consisting of a spacer frame of low-scaling steel which had internal dimensions of 12×12×2.5 cm, lay on a steel sheet and was covered with a steel sheet, the spacer frame and the steel sheets being made of material 8 mm thick, was pressed together by screwing. The mould was talced and assembled horizontally, apart from the steel covering sheet. A 2 mm thick flat sheet of commercially available polyphenylene sulphide was laid in the spacer frame, this sheet was then coated uniformly with 40 g of the mixture consisting of expandable graphite and binder, and finally a second, corresponding sheet of polyphenylene sulphide was placed on top.

After the mould had been closed, it was heated at 420° C. in an oven and then cooled and the sandwich formed was removed from the mould.

It consisted of the two polyphenylene sulphide covering sheets, to which the core material of the expanded expandable graphite mixture was firmly joined. The sandwich had the dimensions of the interior of the mould determined by the spacer frame. The core material had an average density of 0.15 g/cm<sup>3</sup>. In a shearing test, the covering sheet did not become detached from the core material, but the core material broke up.

### Example 2

The procedure was as in Example 1, but a commercially available SO<sub>x</sub> expandable graphite with similar expansion properties was used as the expandable graphite. The expandable graphite was employed without a binder and the heating temperature was increased to 50 620° C.

A sandwich was formed in which the core material had been forced into the covering layer material to the extent that an edge zone of integral character impregnated with the covering layer material was formed. The surface layer consisted of annealed polyphenylene sulphide.

### Example 3

The procedure was as in Example 1, but instead of polyphenylene sulphide a pane of window glass 2.5 mm thick was used as the covering layer on both sides and a heating temperature of 850° C. was used. An aluminium foil was employed as the release agent here. In order to avoid stresses, the product was cooled in the course of 18 hours. A dimensionally accurate sandwich, the covering layers of which were free from cracks and firmly joined to the core material, was removed from the mould. Example 4

The procedure was as in Example 3, but instead of the pane of window glass, a layer of the same amount by weight of glass powder was introduced onto the bottom of the mould and a double layer of desized glass silk fabric in a dense linen weave was laid on top as the top covering layer. After removal from the mould, a sandwich with a crack-free glassy surface was obtained. In this case, the penetration of the core material and covering layer was greater than in Example 3.

#### Example 5

The procedure was as in Example 1, but a powder mixture, predried at 350° C., of 70 parts of aluminium hydroxide and 30 parts of colemanite were introduced into the mould as the bottom layer and as the top layer in a height of in each case 3 mm. In addition to talc, a double layer of packing paper (soda Kraft paper) was employed as the release agent. The heating temperature was 950° C.

After cooling, a sandwich, the bottom covering layer of which consisted of a ceramic sinter layer and the core of which consisted of an expanded expandable graphite mixture having an average bulk density of 0.1 g/cm<sup>3</sup>, obtained.

#### Example 6

The procedure was as in Example 1, but a mixture of 80 parts of SO<sub>x</sub> expandable graphite and 20 parts of neutral ethylenediamine phosphate was used as the expansion material containing a binder. In addition, polycarbonate sheets (Makrolon®) were used instead of polyphenylene sulphide sheets. The heating temperature was 350° C. After removal from the mould, a sandwich sheet having polycarbonate covering layers which were firmly joined to the core material was obtained.

#### Example 7

A 1.5 mm thick layer of NO<sub>x</sub> expandable graphite and a binder (mixture as in Example 1) was sprinkled onto a 2 mm thick, circular sheet of apparatus glass and covered by an identical glass plate in a flush manner. This package was heated up to 850° C. in an oven, a 1.5 cm thick sandwich being formed. The sandwich was then pressed to a hemisphere at 900° C. in a press mould using a hemispherical die, the sandwich structure being retained. After cooling slowly, the moulding was removed from the mould.

#### Example 8

The procedure was analogous to Example 1. However, a mixture of equal parts of a) expandable graphite + binder (mixture as in Example 1) and b) bitumen was introduced between the polyphenylene sulphide covering layers. The heating temperature was 460° C. The resulting sandwich proved to be particularly pressure-resistant.

#### Example 9

The procedure was as in Example 1, but instead of the polyphenylene sulphide sheets, two sheets of identical dimensions made of commercially available aluminium sheet were used and a heating temperature of 680° C. was applied. A sandwich with aluminium covering layers firmly adhering to the core material was obtained.

#### Example 10

The procedure was as in Example 1, but a lentiform depression and writing were milled into the inside of the steel covering sheet. After removal from the mould, the lentil and the writing were imaged on the upper side of the sandwich formed, since the thermoplastic material of the covering layer had been forced by the expansion pressure of the core material into the covering sheet provided with the depression and writing.

#### Example 11

The procedure was as in Example 1, but in each case an aluminium sheet 2 mm thick was used as the top and bottom covering layer and in each case granules of about 3 mm diameter which had been prepared from 70% of NO<sub>x</sub> expandable graphite and 30% of the following binders were used:

- 20 A) binder as in Example 1,
- B) commercially available ammonium polyphosphate (90%) mixed with 10% of cane sugar,
- C) secondary ammonium phosphate (90%) mixed with 10% of carboxymethylcellulose,
- D) neutralization product of ethylenediamine and orthophosphoric acid (90%) mixed with 10% of soluble starch and
- E) no binder, 100% of NO<sub>x</sub> expandable graphite.

In each case 30 g of expandable graphite mixture were poured into the mould and were heated at 600° C. for 30 minutes. After cooling, in each case a sandwich with a firmly adhering covering layer which could be pulled off only with destruction of the core material in the case of A) to D) was removed from the mould.

35 A cuboid of dimensions 2.5×3.0×2.0 cm was cut out of each core material of the sandwich prepared using A) to E) and was introduced into an oven heated at 700° C., with access of air. In all cases, the core material had a specific gravity of about 0.1 g/cm<sup>3</sup>. The stabilisation towards oxidative attack achieved by the phosphorus compounds in the binder was determined as follows from the weight loss after 2 and 3 hours at 700° C.:

	Sample	% loss after	
		2 hours	3 hours
45	A)	5.5	5.5
	B)	16.2	16.2
	C)	13.3	13.4
50	D)	9.9	9.9
	E)	55.4	70.1

55 The particularly good stabilisation of the core material containing the phosphonate binder from Example 1 (sample A)) is striking here.

#### Example 12

A steel cylindrical mould consisting of two half-shells having a total volume of 2.7 l and a diameter of 4.5 cm 60 was filled in the horizontal position with 300 g of granules according to Example 11A), after it had first been lined with 100 µm foils.

The foils used were:

- A) commercial polyimide foil,
- B) polyphenylene sulphide foil,
- C) aluminium foil,
- D) copper foil and
- E) silver foil.

The mould was heated at 600° C. in the horizontal position for 30 minutes and then cooled.

In all cases, a foamed rod firmly laminated with the particular covering layer, the core material of which had a density of about 0.95 g/cm<sup>3</sup>, had formed.

Such a rod material can be used as a semi-finished product for the production of shielding elements for high-performance electronic components.

#### Example 13

The procedure was as in Example 12, a jacket tube of aluminium being used instead of the foil. An impact energy absorption element which is suitable for intercepting axially directed impacts was obtained.

What is claimed is:

- 5 1. A lightweight shaped article comprising a core having a top surface and a bottom surface and at least one covering layer on both the top surface of said core and the bottom surface of said core, wherein at least one of said covering layers is consisting of a thermoplastic material, said core having a bulk density of less than 0.9 g/cm<sup>3</sup>; said core consisting essentially of expanded graphite, a phosphate or phosphonate binder, and optionally a filler; said filler being selected from the group
- 10 consisting of glass, quartz, carbon, chalk, asbestos, flyash, talc, calcined or slaked lime, hydrargillite, cement, kaolin, and mixtures thereof; said binder being present in an amount of 10% to 85% based on the total weight of the shaped article; said filler being present in
- 15 an amount of up to 75% based on the total weight of the shaped article.

\* \* \* \* \*

20

25

30

35

40

45

50

55

60

65

# United States Patent [19]

Howard

[11] Patent Number: 4,961,991

[45] Date of Patent: Oct. 9, 1990

## [54] FLEXIBLE GRAPHITE LAMINATE

[75] Inventor: Ronald A. Howard, Brook Park, Ohio

[73] Assignee: Ucar Carbon Technology Corporation, Danbury, Conn.

[21] Appl. No.: 471,531

[22] Filed: Jan. 29, 1990

[51] Int. Cl. 5 ..... B32B 31/06

[52] U.S. Cl. .... 428/246; 277/227;  
277/DIG. 6; 428/251; 428/408; 428/421;  
428/422

[58] Field of Search ..... 428/246, 251, 408, 421,  
428/422; 277/DIG. 6, 227

## [56] References Cited

### U.S. PATENT DOCUMENTS

4,822,062 4/1989 Gallo et al. ..... 277/235

## FOREIGN PATENT DOCUMENTS

248785 12/1983 Japan

## OTHER PUBLICATIONS

GRAFOIL ® Flexible Graphite Sales Literature of UCAR Carbon Company Inc.

GRAFOIL ® Flexible Graphite Design Data Sales Literature of UCAR Carbon Inc.

Primary Examiner—James J. Bell

Attorney, Agent, or Firm—Cornelius F. O'Brien

## [57] ABSTRACT

A flexible graphite laminate suitable for use as gaskets in which a polymer resin coated cloth, such as polytetrafluoroethylene coated fiber glass cloth, is disposed and bonded between two sheets of flexible graphite material. A method for producing the flexible graphite laminate is also disclosed.

10 Claims, No Drawings

## FLEXIBLE GRAPHITE LAMINATE

### FIELD OF THE INVENTION

The invention relates to flexible graphite laminates suitable for use as gaskets, said laminates containing a polymer resin coated cloth dispersed and bonded between two sheets of flexible graphite material.

### BACKGROUND OF THE INVENTION

A wide variety of flexible graphite laminates are manufactured for use as gaskets for various applications. Some of the laminates contain metal or plastic sheets bonded between two sheets of flexible graphite material. The plastic or metal interlayer is used to increase the strength and ease of handling of the laminate during cutting to form gaskets and to give strength to the gaskets when they are put in place for use. The use of a metal interlayer also improves the resistance of the gasket to blowout and reduces high temperature creep of the gasket when exposed to a high temperature environment. The metal interlayer gaskets are extremely strong; however, cutting the laminate will expose sharp edges which can present a hazard to personnel handling the gasket.

Japanese Patent Application No. 1983-248,785 discloses gasket materials in which a metal net is disposed and sealed within two sheets of flexible graphite. The metal net is employed as a reinforcing material since graphite sheets when used alone as a gasket have problems in that the strength of the gasket is weak. The gasket material is prepared by arranging a flexible graphite sheet obtained by cold-working graphite commonly known as expanded graphite, on both sides of a metal net and then press-adhering the graphite to the metal net.

It is an object of the present invention to provide flexible graphite laminates suitable for use as gaskets having excellent resistance to interlaminar leakage.

It is another object of the present invention to provide flexible graphite gaskets comprising a polymer resin coated cloth disposed and bonded between two sheets of flexible graphite material.

It is another object of the present invention to provide a flexible graphite gasket comprising a polytetrafluoroethylene coated woven fiber glass cloth disposed and so bonded between two sheets of flexible graphite material.

It is another object of the present invention to provide a method for producing flexible graphite laminates comprising a polymer resin coated cloth disposed and bonded between two sheets of flexible graphite material.

Additional objects of the invention will become evident from the description that follows.

### SUMMARY OF THE INVENTION

The invention relates to a flexible graphite laminate comprising a polymer resin coated cloth disposed and bonded between two sheets of flexible graphite material.

As used herein a cloth is a pliable fabric made usually by weaving, felting or knitting natural or synthetic fibers and filaments. The flexible graphite laminate of this invention has high strength, good handling characteristics and good resistance to interlaminar leakage. In a preferred embodiment, the polymer resin would be

polytetrafluoroethylene and the cloth would be fiber glass and the graphite would be flexible graphite.

The invention also relates to a method for producing a flexible graphite laminate comprising the steps:

- 5     (a) placing a polymer resin coated cloth between two sheets of flexible graphite; and
- (b) pressing the sheets of flexible graphite together while heating to a temperature sufficient to soften the polymer resin thereby bonding together the polymer resin coated cloth between the two sheets of flexible graphite to produce a flexible graphite laminate.

The flexible graphite laminate produced can be cut into gaskets that will have good strength and handling characteristics and have no sharp edges. In addition, the

15     laminate produced gaskets will have good resistance to blowout and high-temperature creep. The cloth for use in this invention could be woven or nonwoven fabric made of ceramic fibers such as fiber glass, Al<sub>2</sub>O<sub>3</sub> or SiC, or carbon fibers such as graphite. The coated cloth

20     could be a non-porous or porous cloth and vary in thickness from 0.0005 inch to about 0.020 inch with a thickness of from 0.002 inch to 0.005 inch being preferred for most gasket applications. Some suitable cloths are fiber glass, alumina, zirconia, carbon, or any

25     high temperature polymer. The preferred polymer resins for use in this invention are resins such as polytetrafluoroethylene, aramides, polyamides, polyimidemides, polyesters, polyimides and the like. The specific resin selected could be thermoplastic or thermosetting and

30     should be one that will be suitable for the environment in which the laminate will be used. An example of a thermosetting resin is a phenolic or polyester resin. Preferably, the polymer resin could be thermoplastic so that when coated onto the surface of a suitable cloth

35     and subjected to a high temperature environment, the polymer resin will soften so that it can then be bonded between two sheets of graphite material using a suitable amount of pressure.

The high temperature environment used should be sufficient to soften the polymer resin and permit the coated cloth to be pressure bonded between two sheets of flexible graphite. Generally, a temperature between about 80° C. and 400° C. would be suitable for most thermoplastic polymer resins. The preferred polymer resin is polytetrafluoroethylene which should

40     preferably be heated from about 350° C. to 370° C. The pressure applied to the laminate while the resin is soft shall be sufficient to insure good contact and bond between the layers of the flexible graphite. Generally a pressure of about 50 pounds per square inch or more would be sufficient for most applications. If the polymer resin selected is not thermoplastic, then a suitable adhesive such as a chloroprene rubber may be used to bond the filled cloth between the graphite sheets. However, if a thermosetting resin is used, then in some applications,

45     it could be used in the "B stage" condition so that an adhesive would not be necessary. The adhesive, when used, must be one that will bond to the polymer resin selected. The polymer resin is primarily used to fill and coat the cloth so that not only are the fibers coated but

50     also any space between the fibers are completely filled with the resin. This will produce a non-porous cloth that will insure that no interlaminar leakage will occur in the laminate structure thereby insuring that when the laminate is used as a gasket, it will have minimum leakage.

The flexible graphite preferred for use in the laminate of this invention is flexible graphite sheet material produced as described in U.S. Pat. No. 3,404,061. Specifi-

cally the process comprises treating flake graphite particles with a suitable oxidizing medium to form soggy graphite particles which are heated to permit a natural expansion and then compressed or compacted together, in the absence of any binder, so as to form a flexible integrated graphite sheet of desired thickness and density. The compression or compaction is carried out by passing a thick bed of expanded particles between pressure rolls or a system of multiple pressure rolls to compress the material in several stages into sheet material of desired thickness. The compression operation flattens the expanded graphite particles causing them to engage and interlock. However, if the compressive force applied to the particles is excessive, the particles split and separate causing weak spots which puncture to form pinholes when forming very thin sheets. Accordingly, the sheet thickness was heretofore substantially limited to a thickness in excess of about ten mils. One recent proposal for forming thin sheet graphite material with a thickness equal to ten mils without forming pinholes is described in Japanese patent publication application No. 61(1986)-133865 entitled Method For Producing Flex Graphite Sheet. According to the Japanese publication a thin graphite sheet can be formed without pinholes by applying an adhesive layer and expanded graphite on a polyester film, metal foil or paper tape before the graphite sheet is rolled down to the desired thickness of ten mils.

U.S. application Ser. No. 373,914 titled Ultra-thin Pure Flexible Graphite, describes that a sheet of ultra-thin graphite of below ten mils in thickness can be formed without pinholes from natural graphite particles by increasing the degree of expansion of the particles during the exfoliation operation to produce particles which, prior to compression, have been expanded to a specific volume of at least 450 cc/gm. By causing the exfoliated graphite particles to expand before compression to at least this minimum specific volume substantially reduces the susceptibility of forming pinholes during compression of the particles into ultra-thin sheet material of below 8 mils in thickness and particularly between 1-4 mils in thickness with a high degree of area/weight uniformity. The process disclosed in this application is applicable primarily to natural graphite particles.

For most gasket applications, the flexible graphite sheet should be from 0.002 inch to 0.080 inch thick and preferably from 0.005 inch to 0.060 inch thick. The cloth for gasket application can be from 0.0005 inch to 0.020 inch thick and preferably from 0.002 inch to 0.005 inch thick. The overall laminate for use in most gasket applications can be from 0.0045 inch to 0.180 inch thick and preferably from 0.012 inch to 0.125 inch thick. The polymer resin should be applied to coat at least the fibers and preferably also any spaces between the fibers so that the cloth is non-porous. There should be sufficient excess resin on the surface of the cloth to insure that bonding to the flexible graphite sheets will take place. As stated above, if the polymer resin is thermoplastic, then it can serve to bond the graphite sheets of the laminate together. If the polymer resin is not a thermoplastic resin or a "B stage" thermosetting resin, then a suitable adhesive could preferably be used to bond the cloth between the flexible graphite sheets.

The preferred laminate for use as gaskets would comprise a fiber glass cloth coated and filled with polytetrafluoroethylene and then pressure bonded between two sheets of flexible graphite sheets. A preferred flexible

graphite sheet material is sold by UCAR Carbon Company Inc under the trademark Grafoil which is registered to UCAR Carbon Technology Corporation.

#### EXAMPLE

Two variations of flexible graphite laminates were produced as follows. The first variety (Sample A) comprised a polytetrafluoroethylene coated fiber glass cloth dispersed between two sheets of Grafoil flexible graphite. The polytetrafluoroethylene coated the fiber glass threads and bonded the weave together but did not fill the spaces between the threads so that the cloth was porous. The coated cloth was 2.5 mils thick and each of the sheets of flexible graphite was 30 mils thick. The laminate was hot-bonded at a temperature between 300° C. and 325° C. at a pressure from 50 to 300 pounds per square inch. This high temperature softened the polytetrafluoroethylene and under the applied pressure, the polytetrafluoroethylene bonded the cloth between the flexible graphite sheets. The laminate was cut to produce a gasket ring with a 90 mm outside diameter and a 50 mm inside diameter. The edge of the gasket ring was smooth.

A second variety (Sample B) was made the same way except that additional polytetrafluoroethylene was used to fill all the voids and spaces in the fiber glass cloth so that the cloth was non-porous. This second variety could also be thought of as a solid sheet of polytetrafluoroethylene in which the fiber glass cloth was used as an internal reinforcement.

The two gaskets were tested for sealability according to the DIN 3535 sealability test which is a test generally employed in West Germany and to some degree in other European countries and the United States. Specifically, nitrogen gas at 580 pounds per square inch (40 bars) was introduced to the center of the gaskets while the gaskets were clamped under a force of 1000 pounds per square inch. The gas leak rate in ml/min was then measured through the gasket. The clamping force is then increased in stages up to 4600 pounds per square inch and the leak rate was measured at each stage. The results of the test are shown in the Table.

TABLE

	Sample Gasket A	Sample Gasket B		
	Clamping Load (psi)	Leak Rate (ml/min)	Clamping Load (psi)	Leak Rate (ml/min)
1000	66	1000	18	
1500	61	1500	17	
2000	52	2000	14	
2500	42	2500	9	
4600	18	4600	3	

The results of the data show that the use of a non-porous gasket of polytetrafluoroethylene coated and filled fiber glass interlayer dramatically improved the sealability over a porous gasket.

While in the foregoing specification a detailed description of specific embodiments of the invention was set forth for the purpose of illustration, it is to be understood that many of the details herein given may be varied considerably by those skilled in the art without departing from the spirit and scope of the invention.

What is claimed:

1. A flexible graphite laminate comprising a polymer resin coated cloth disposed and bonded between two sheets of flexible graphite material.

2. The flexible graphite laminate of claim 1 wherein the polymer resin is thermoplastic.

3. The flexible graphite laminate of claim 1 wherein the polymer resin is selected from the group consisting of polytetrafluoroethylene, aramide, polyamides, polyimidemides, polyesters and polyimides

4. The flexible graphite laminate of claim 2 wherein the polymer resin is polytetrafluoroethylene.

5. The flexible graphite laminate of claim 1 wherein the cloth is made from fibers selected from the group consisting of ceramic fibers and carbon fibers.

6. The flexible graphite laminate of claim 5 wherein the cloth is fiber glass.

7. The flexible graphite laminate of claim 1 wherein the laminate is a gasket.

8. The flexible graphite laminate of claim 7 wherein the gasket is from 0.0045 to 0.180 inch thick.

9. The flexible graphite laminate of claim 7 wherein the polymer resin is polytetrafluoroethylene and the cloth is fiber glass.

10. The flexible graphite laminate of claim 9 wherein the gasket is from 0.0045 inch to 0.180 inch thick.

\* \* \* \* \*

15

20

25

30

35

40

45

50

55

60

65

**UNITED STATES PATENT AND TRADEMARK OFFICE**  
**Certificate**

Patent No. 4,961,991

Patented: Oct. 9, 1990

On petition requesting issuance of a certificate for correction of inventorship pursuant to 35 U.S.C. 256, it has been found that the above-identified patent, through error and without any deceptive intent, improperly sets forth the inventorship.

Accordingly, it is hereby certified that the correct inventorship of this patent is: Ronald A. Howard and James J. Polomsky.

Signed and Sealed this 16th Day of April, 1991.

GEORGE F. LESMES

*Supervisory Patent Examiner  
Art Unit 154*



US 20010041253A1

(19) United States

(12) Patent Application Publication

Mercuri et al.

(10) Pub. No.: US 2001/0041253 A1

(43) Pub. Date: Nov. 15, 2001

(54) FLEXIBLE GRAPHITE ARTICLE AND  
METHOD OF MANUFACTURE

(76) Inventors: Robert Angelo Mercuri, Seven Hills,  
OH (US); Joseph Paul Capp,  
Strongsville, OH (US); Michael Lee  
Wardrip, Parma, OH (US); Thomas  
William Weber, Cleveland, OH (US)

Correspondence Address:

James R. Cartiglia  
Graftech Inc.  
Suite 1100  
3102 West End Avenue  
Nashville, TN 37203 (US)

(21) Appl. No.: 09/906,281

(22) Filed: Jul. 16, 2001

Related U.S. Application Data

(62) Division of application No. 09/548,118, filed on Apr.  
12, 2000.

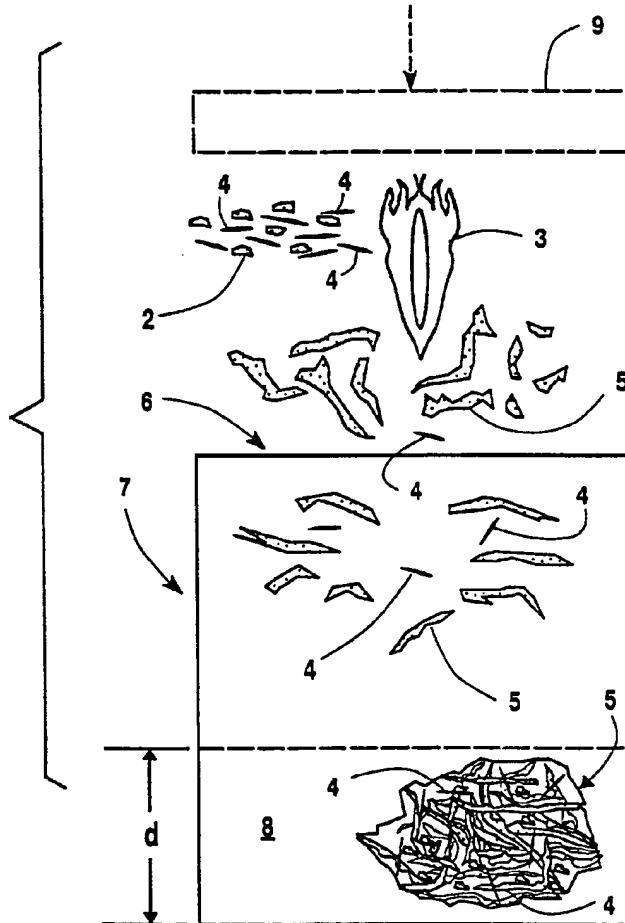
Publication Classification

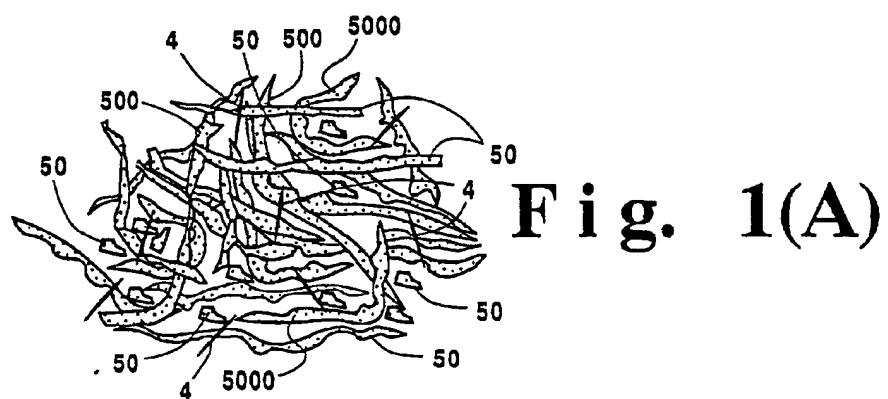
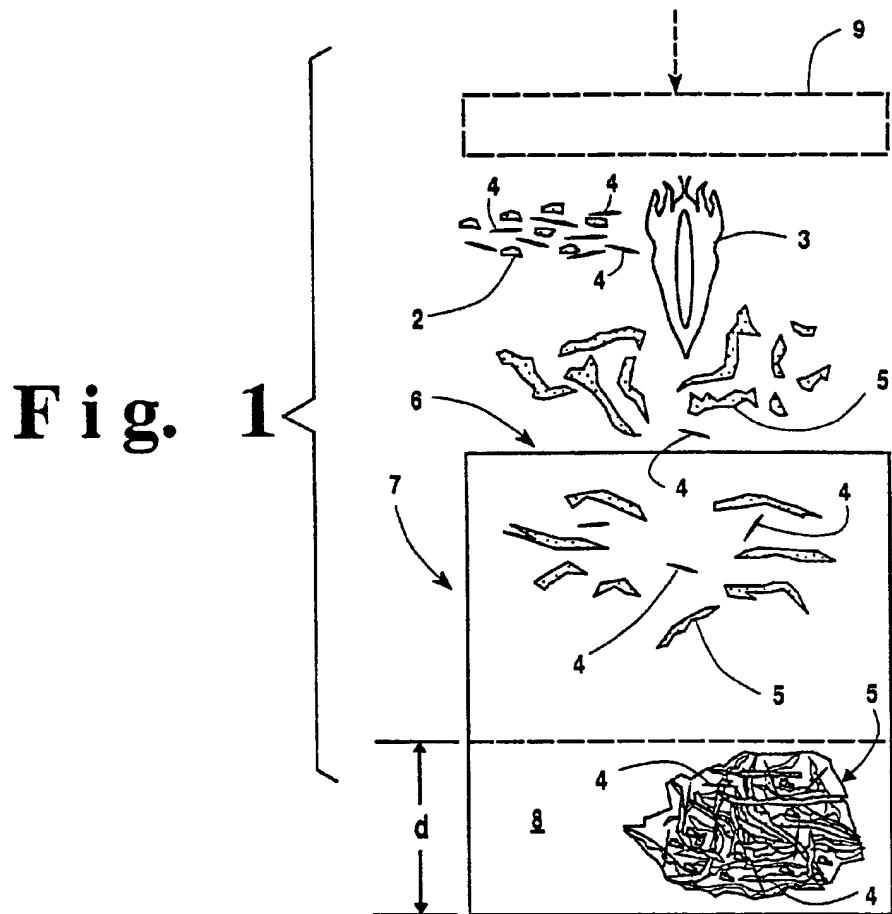
(51) Int. Cl. 7 ..... B29C 47/00; B32B 1/00;  
B29C 41/00; B29C 39/22;  
B05D 3/02

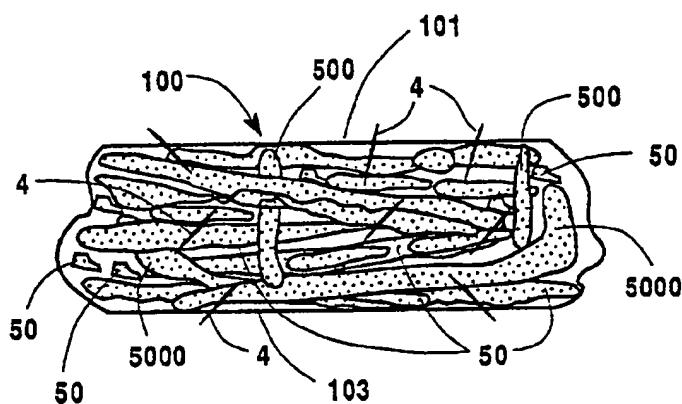
(52) U.S. Cl. ..... 428/220; 428/332; 427/372.2;  
264/176.1; 264/299

(57) ABSTRACT

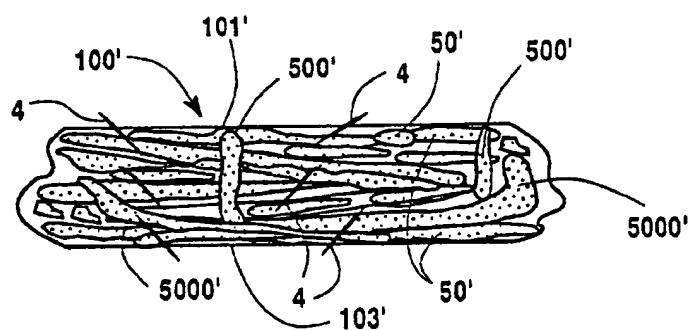
A flexible graphite sheet exhibiting enhanced isotropy is provided. In addition, an apparatus, system and method for continuously producing a resin-impregnated flexible graphite sheet is also provided.



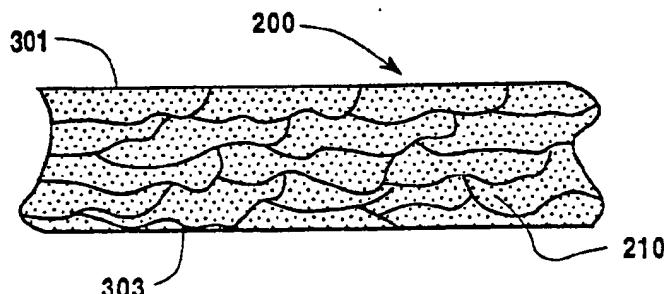




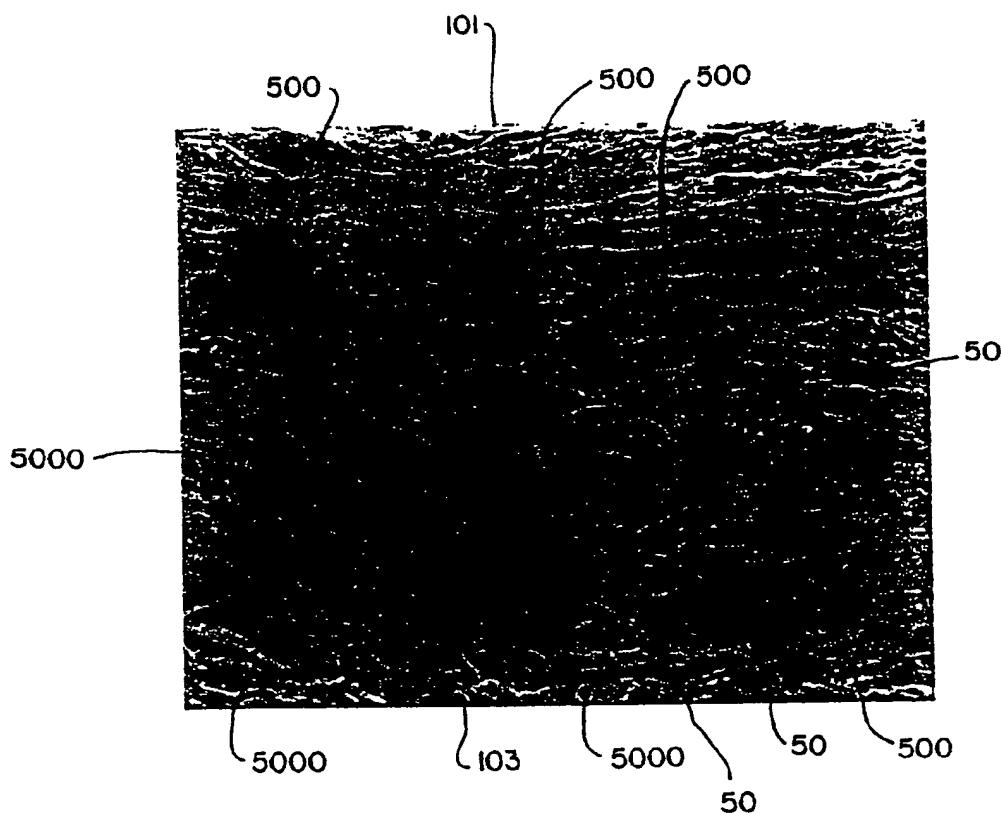
**F i g. 2**



**F i g. 2(A)**

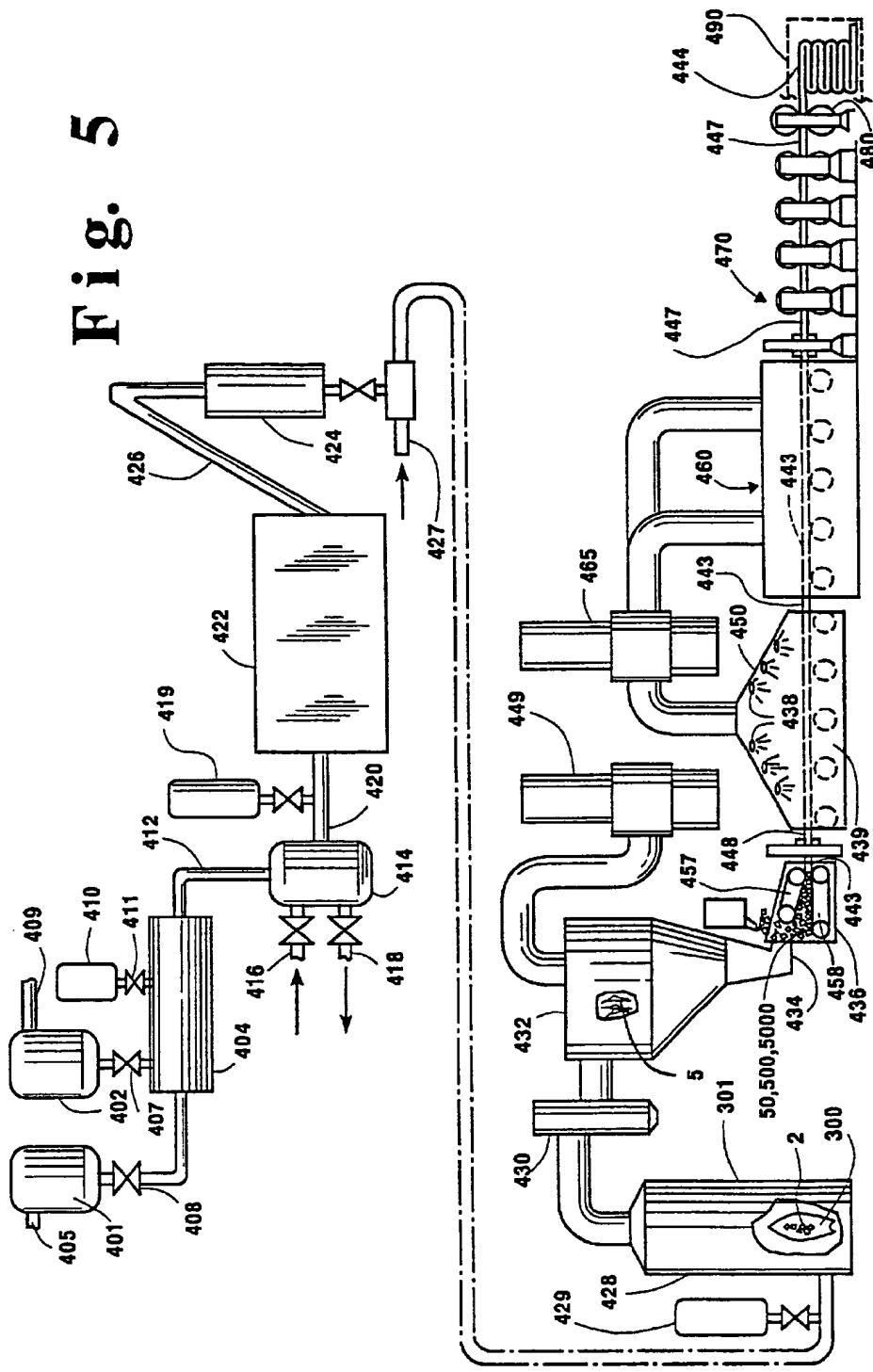


**F i g. 3**



F i g. 4

5  
50  
•  
E



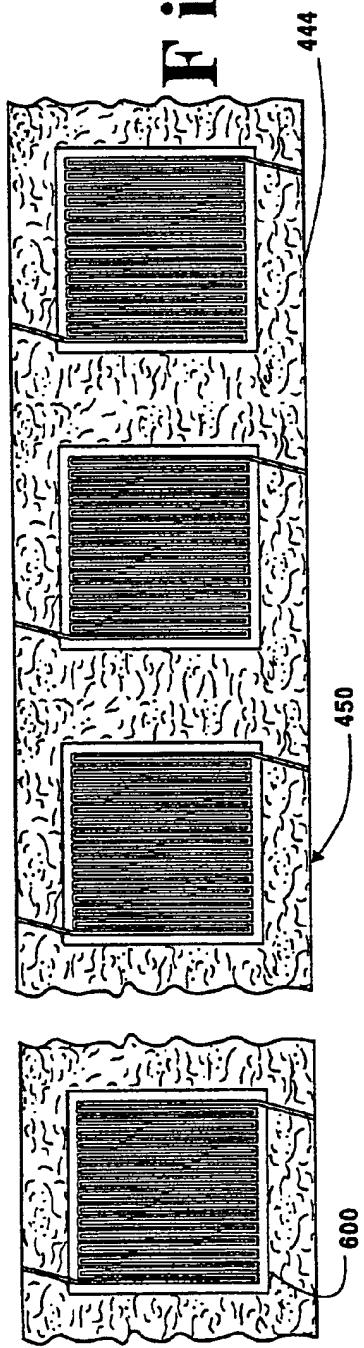
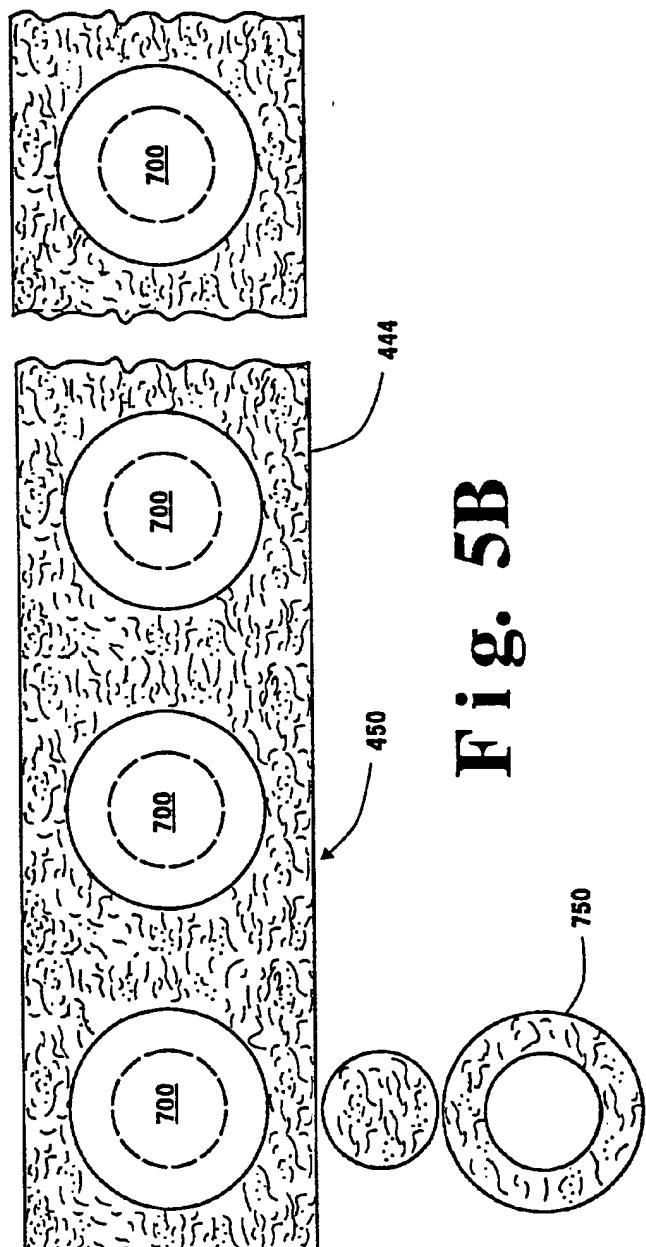
**Fig. 5A****Fig. 5B**

Fig. 5D

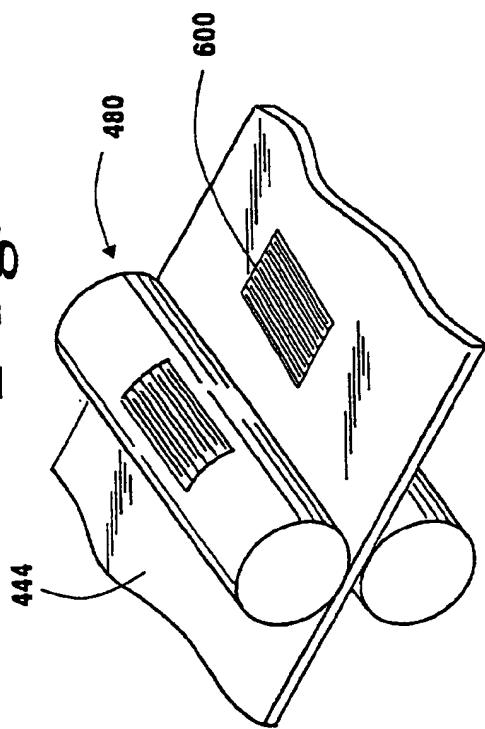
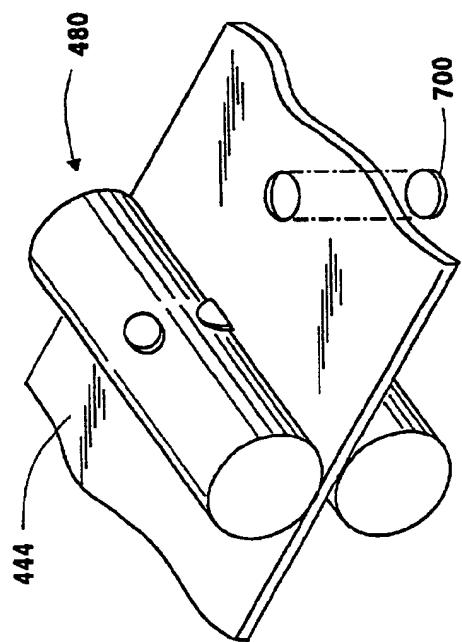


Fig. 5C



## FLEXIBLE GRAPHITE ARTICLE AND METHOD OF MANUFACTURE

### TECHNICAL FIELD

[0001] The present invention relates to planar flexible graphite articles, such as flexible graphite sheet, and to a system and method for continuously producing such articles. More particularly, the present invention relates to flexible graphite sheet material that exhibits enhanced isotropy with respect to thermal and electrical conductivity and fluid diffusion, as well as to a method for producing the sheet.

### BACKGROUND OF THE INVENTION

[0002] Graphites are made up of layer planes of hexagonal arrays or networks of carbon atoms. These layer planes of hexagonally arranged carbon atoms are substantially flat and are oriented or ordered so as to be substantially parallel and equidistant to one another. The substantially flat, parallel equidistant sheets or layers of carbon atoms, usually referred to as basal planes, are linked or bonded together and groups thereof are arranged in crystallites. Highly ordered graphites consist of crystallites of considerable size: the crystallites being highly aligned or oriented with respect to each other and having well ordered carbon layers. In other words, highly ordered graphites have a high degree of preferred crystallite orientation. It should be noted that graphites possess anisotropic structures and thus exhibit or possess many properties that are highly directional, e.g., thermal and electrical conductivity and fluid diffusion. Briefly, graphites may be characterized as laminated structures of carbon, that is, structures consisting of superposed layers or laminae of carbon atoms joined together by weak van der Waals forces. In considering the graphite structure, two axes or directions are usually noted, to wit, the "c" axis or direction and the "a" axes or directions. For simplicity, the "c" axis or direction may be considered as the direction perpendicular to the carbon layers. The "a" axes or directions may be considered as the directions parallel to the carbon layers or the directions perpendicular to the "c" direction. The natural graphites suitable for manufacturing flexible graphite possess a very high degree of orientation.

[0003] As noted above, the bonding forces holding the parallel layers of carbon atoms together are only weak van der Waals forces. Graphites, especially natural graphites, can be treated so that the spacing between the superposed carbon layers or laminae can be appreciably opened up so as to provide a marked expansion in the direction perpendicular to the layers, that is, in the "c" direction and thus form an expanded or intumesced graphite structure in which the laminar character of the carbon layers is substantially retained.

[0004] Natural graphite flake which has been expanded and more particularly expanded so as to have a final thickness or "c" direction dimension which is at least about 80 or more times the original "c" direction dimension can be formed without the use of a binder into cohesive or integrated sheets, e.g., webs, papers, strips, tapes, or the like. The formation of graphite particles which have been expanded to have a final thickness or "c" dimension which is at least 80 times the original "c" direction dimension into integrated sheets by compression, without the use of any binding material is possible. It is believed that this is due to

the excellent mechanical interlocking, or cohesion that is achieved between the voluminously expanded graphite particles.

[0005] In addition to flexibility, the sheet material, as noted above, has also been found to possess a high degree of anisotropy with respect to thermal and electrical conductivity and fluid diffusion, comparable to the natural graphite starting material due to orientation of the expanded graphite particles substantially parallel to the opposed faces of the sheet resulting from very high compression, such as roll pressing. Sheet material thus produced has excellent flexibility, good strength and a very high degree of orientation.

[0006] Briefly, the process of producing flexible, binderless anisotropic graphite sheet material comprises compressing or compacting under a predetermined load and preferably in the absence of a binder, expanded graphite particles which have a "c" direction dimension which is at least 80 times that of the original particles so as to form a substantially flat, flexible, integrated graphite sheet. The expanded graphite particles are generally worm-like or vermiform in appearance, and once compressed, will maintain the compression set and alignment with the opposed major surfaces of the sheet. The density and thickness of the sheet material can be varied by controlling the degree of compression. The density of the sheet material can be within the range of from about 5 pounds per cubic foot to about 125 pounds per cubic foot. The flexible graphite sheet material exhibits an appreciable degree of anisotropy due to the alignment of graphite particles parallel to the major opposed, parallel surfaces of the sheet, with the degree of anisotropy increasing upon roll pressing of the sheet material to increased density. In roll pressed anisotropic sheet material, the thickness, i.e. the direction perpendicular to the opposed, parallel sheet surfaces comprises the "c" direction and the directions ranging along the length and width, i.e., along or parallel to the opposed, major surfaces comprises the "a" directions and the thermal, electrical and fluid diffusion properties of the sheet are very different, by orders of magnitude, for the "c" and "a" directions.

[0007] This very considerable difference in properties, i.e., anisotropy, which is directionally dependent, can be disadvantageous in some applications. For example, in gasket applications where flexible graphite sheet is used as the gasket material and in use is held tightly between metal surfaces, the diffusion of fluid like gases or liquids occurs more readily parallel to and between the major surfaces of the flexible graphite sheet. It would, in most instances, provide for greater gasket performance, if the resistance to fluid flow parallel to the major surfaces of the graphite sheet ("a" direction) were increased, even at the expense of reduced resistance to fluid diffusion flow transverse to the major faces of the graphite sheet ("c" direction). With respect to electrical properties, the resistivity of anisotropic flexible graphite sheet is high in the direction transverse to the major surfaces ("c" direction) of the flexible graphite sheet, and very substantially less in the direction parallel to and between the major faces of the flexible graphite sheet ("a" direction). In applications such as seals or other components (such as fluid flow field plates or gas diffusion layers) of fuel cells, it would be of advantage if the electrical resistance transverse to the major surfaces of the flexible graphite sheet ("c" direction) were decreased, even at the

expense of an increase in electrical resistivity in the direction parallel to the major faces of the flexible graphite sheet ("a" direction).

[0008] With respect to thermal properties, the thermal conductivity of a flexible graphite sheet in a direction parallel to the upper and lower surfaces of the flexible graphite sheet is relatively high, while it is relatively very low in the "c" direction transverse to the upper and lower surfaces. At times, and in certain applications, such as thermal interfaces, it may be desirable to increase the thermal conductivity of the sheet in the "c" direction.

[0009] In some applications, it is important to incorporate additives in the flexible graphite sheet in order to achieve corrosion resistance and to impregnate the flexible graphite sheet with resins and/or other material to increase the strength and water resistance of the flexible graphite sheet. Also, it is important at times to provide such additives in the course of processing the natural graphite into flexible graphite.

[0010] These foregoing situations are accommodated by the present invention.

#### SUMMARY OF THE INVENTION

[0011] In accordance with the present invention, a flexible graphite article in the form of a sheet having opposed, relatively planar, major surfaces is provided. The article is formed of particles of expanded (or exfoliated) graphite, an optically detectable portion of which, at magnifications of 100 $\times$  or less, are substantially unaligned with the opposed planar major surfaces of the flexible graphite article. Preferably, at least a portion of the unaligned particles are transverse to the opposed major surfaces of the article. The flexible graphite article is characterized by having decreased electrical resistivity and increased thermal conductivity in a direction transverse to the opposed planar major surfaces of the flexible graphite sheet and increased resistance to fluid flow in a direction parallel to the opposed planar major faces of the flexible graphite sheet. The flexible graphite sheet, with or without additives and/or impregnants, can be mechanically altered, such as by embossing, die molding and cutting to form components for electrochemical fuel cells, gaskets and heat conducting and heat resistant articles.

[0012] The present invention also includes an apparatus, system and method for producing flexible graphite sheet articles, such as those having decreased electrical resistivity and increased thermal conductivity in a direction transverse to the opposed planar major surfaces of the flexible graphite sheet and increased resistance to fluid flow in a direction parallel to the opposed planar major faces of the flexible graphite sheet.

[0013] The inventive method comprises reacting raw graphite particles with a liquid intercalant solution to form intercalated graphite particles; exposing the intercalated graphite particles to a temperature of at least about 700° C. to expand the intercalated graphite particles to form a stream of exfoliated graphite particles; continuously compressing the stream of exfoliated graphite particles into a continuous coherent self-supporting mat of flexible graphite; continuously contacting the flexible graphite mat with liquid resin and impregnating the mat with liquid resin; and continuously calendering the flexible graphite mat to increase the

density thereof to form a continuous flexible graphite sheet having a density of from about 5 to about 125 lbs/ft<sup>3</sup> and a thickness of from about 1.0 to 0.003 inches.

[0014] The method also advantageously includes mechanically deforming a surface of the continuous flexible graphite sheet to provide a series of repeating patterns on a surface of the flexible graphite sheet or the removal of material from the flexible graphite sheet in a series of repeating patterns and vaporizing at least some of the solvent from the resin prior to mechanically deforming a surface of the continuous flexible graphite sheet.

[0015] As noted, the present invention also includes an apparatus for the continuous production of resin-impregnated flexible graphite sheet, comprising a reactor vessel for containing as reactants graphite particles in mixture with a liquid intercalant solution to form intercalated graphite particles; an expansion chamber in operative connection with the reactor vessel, the interior of the expansion chamber being at a temperature of at least about 700° C. (and preferably enclosing an open flame), such that passing intercalated graphite particles from the reactor vessel to the expansion chamber causes expansion of the intercalated graphite particles to form exfoliated graphite particles; a compression station positioned to receive exfoliated graphite particles for compressing such particles into a coherent self-supporting mat of flexible graphite; an impregnation chamber for contacting the flexible graphite mat with liquid resin and impregnating the mat with the liquid resin; a calender mill disposed to receive the flexible graphite mat for increasing the density of the mat to form a continuous flexible graphite sheet preferably having a density of from about 5 to about 125 lbs/ft<sup>3</sup> and a thickness of no more than about 1.0 inches, more preferably about 1.0 to about 0.003 inches.

[0016] The inventive apparatus also preferably includes a device for mechanically deforming a surface of the continuous flexible graphite sheet to provide a series of repeating patterns on a surface of the flexible graphite sheet or the removal of material from the flexible graphite sheet in a series of repeating patterns. It further advantageously has an oven for receiving the mat from the device for mechanically deforming a surface of the continuous flexible graphite sheet, to cure the resin with which the continuous flexible graphite sheet is impregnated.

[0017] In a particular embodiment of the invention, a system for the continuous production of surface patterned, resin-impregnated flexible graphite sheet is presented. The system includes:

[0018] (i) a reactor vessel for containing as reactants raw natural graphite flake-like particles in mixture with sulfuric and nitric acids;

[0019] (ii) an acid containing vessel communicating with said reactor vessel for the introduction of a mixture of sulfuric and nitric acid into said reactor vessel;

[0020] (iii) a graphite particle containing vessel for the introduction of graphite particles into the reactor vessel;

[0021] (iv) a first additive containing vessel communicating with said reactor vessel for the introduction of intercalation enhancing materials, acids or organic chemicals;

0.08-2.00  
g/cc

- [0022] (v) a wash vessel containing water communicating with the reactor vessel to receive reaction product in the form of acid intercalated graphite particles and remove acid from the surface of the acid intercalated graphite particles and a portion of the mineral impurities contained in the natural graphite particles introduced into the reactor vessel;
- [0023] (vi) a drying chamber for drying washed acid intercalated graphite particles;
- [0024] (vii) conduit means extending from said wash vessel to said drying chamber for passing washed acid intercalated graphite particles from the wash vessel to the drying chamber;
- [0025] (viii) a second additive containing vessel communicating with the conduit means of (vii) for adding pollution reducing chemicals to the washed, intercalated graphite particles to the washed acid intercalated graphite particles;
- [0026] (ix) a collecting vessel for collecting washed acid intercalated graphite particles admixed with pollution reducing chemicals;
- [0027] (x) conduit means extending from said drying chamber to said collecting vessel for passing acid intercalated graphite particles admixed with acid additives from said drying chamber to said collecting vessel;
- [0028] (xi) a third additive containing vessel communicating with said conduit of (x) for the introduction of ceramic fiber particles in the form of macerated quartz glass fibers, carbon and graphite fibers, zirconia, boron nitride, silicon carbide and magnesia fibers, naturally occurring mineral fibers such as calcium metasilicate fibers, calcium aluminum silicate fibers, aluminum oxide fibers and the like into said conduit and the admixing and entrainment thereof with acid intercalated graphite particles passing from the washing vessel to the drying chamber;
- [0029] (xii) an expansion chamber enclosing an open flame at a temperature of 800 to 1300° C.;
- [0030] (xiii) conduit means extending from said collecting vessel to said expansion chamber for passing dried acid intercalated graphite particles admixed with ceramic particles to said expansion chamber;
- [0031] (xiv) gas inlet means communicating with the conduit means of (xii) for entraining the acid intercalated graphite particles admixed with ceramic particles in a stream of non-reactive gas and passing the entrained acid intercalated graphite particles admixed with ceramic particles into the open flame enclosed in said expansion chamber to cause expansion of the acid intercalated graphite particles of at least about 80 times to form vermicular elongated graphite particles;
- [0032] (xv) a collecting hopper for receiving said vermicular elongated graphite particles admixed with ceramic particles;
- [0033] (xvi) a separator vessel interposed between the expansion chamber and the collecting hopper to collect by gravity separation heavy solid mineral impurity particles from the mixture of vermicular graphite particles with ceramic particles;
- [0034] (xvii) a gas scrubber communicating with said collecting hopper to collect gases generated in the expansion chamber;
- [0035] (xviii) a compression chamber positioned to receive vermicular graphite particles mixed with ceramic fiber particles for compressing said vermicular particles mixed with ceramic particles into a coherent self-supporting mat of flexible graphite from about 1 to about 0.015 inches in thickness and having a density of from about 5 to about 25 lbs./ft.<sup>3</sup>;
- [0036] (xix) an impregnation chamber for contacting the flexible graphite mat of (xviii) with liquid resin and impregnating said flexible graphite with liquid resin;
- [0037] (xx) a dryer disposed to receive the impregnated flexible graphite mat of (xix) and heat and dry said mat;
- [0038] (xxi) a calender mill disposed to receive the flexible graphite mat of (xix) for increasing the density of said flexible graphite mat to form a continuous flexible graphite sheet having a density of from about 5 to about 80 lbs./ft.<sup>3</sup>, a thickness of from about 0.5 to about 0.005 inches and relatively evenly spaced apart opposite surfaces;
- [0039] (xxii) a device for mechanically deforming a surface of the continuous flexible graphite sheet of (xxi) to provide a series of repeating patterns on said surface flexible graphite sheet or the removal of material from said flexible graphite sheet in a series of repeating patterns; and
- [0040] (xxiii) an oven for receiving the mat from the dryer of (xxii) to cure the resin the mat.

#### BRIEF DESCRIPTION OF THE DRAWINGS

- [0041] FIGS. 1, 1(A) show the making of a mass of un-aligned expanded graphite particles;
- [0042] FIGS. 2, 2(A) show planar bodies of flexible graphite having portions of un-aligned graphite particles;
- [0043] FIG. 3 shows a planar body of flexible graphite that does not have portions of un-aligned graphite particles;
- [0044] FIG. 4 is a photograph (original magnification 100 $\times$ ) of a planar body of flexible graphite that corresponds to the sketch of FIG. 2;
- [0045] FIG. 5 shows a system for the continuous production of mechanically deformed planar flexible graphite articles;
- [0046] FIGS. 5(A) and 5(B) show different types of the flexible graphite articles noted above; and
- [0047] FIGS. 5(C) and 5(D) show conventional mechanisms for producing different types of flexible graphite articles noted above.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

- [0048] Graphite is a crystalline form of carbon comprising atoms covalently bonded in flat layered planes with weaker

bonds between the planes. By treating particles of graphite, such as natural graphite flake, with an intercalant of, e.g., a solution of sulfuric and nitric acid, the crystal structure of the graphite reacts to form a compound of graphite and the intercalant. The treated particles of graphite are often referred to as "particles of intercalated graphite." Upon exposure to high temperature, the particles of intercalated graphite expand in dimension as much as about 80 or more times its original volume in an accordion-like fashion in the "c" direction, i.e., in the direction perpendicular to the crystalline planes of the graphite. The exfoliated graphite particles are vermiform in appearance, and are therefore commonly referred to as worms. The worms may be compressed together into flexible sheets that, unlike the original graphite flakes, can be formed and cut into various shapes.

[0049] A common method for manufacturing graphite sheet or foil is described by Shane et al. in U.S. Pat. No. 3,404,061, the disclosure of which is incorporated herein by reference. In the typical practice of the Shane et al. method, natural graphite flakes are intercalated by dispersing the flakes in a solution containing an oxidizing agent of, for instance, a mixture of nitric and sulfuric acid. The intercalation solution contains oxidizing and other intercalating agents known in the art. Examples include those containing oxidizing agents and oxidizing mixtures, such as solutions containing nitric acid, potassium chlorate, chromic acid, potassium permanganate, potassium chromate, potassium dichromate, perchloric acid, and the like, or mixtures, such as for example, concentrated nitric acid and chlorate, chromic acid and phosphoric acid, sulfuric acid and nitric acid, or mixtures of a strong organic acid, e.g. trifluoroacetic acid, and a strong oxidizing agent soluble in the organic acid.

[0050] In a preferred embodiment, the intercalating agent is a solution of a mixture of sulfuric acid, or sulfuric acid and phosphoric acid, and an oxidizing agent like nitric acid, perchloric acid, chromic acid, potassium permanganate, hydrogen peroxide, iodic or periodic acids, or the like. Although less preferred, the intercalation solutions may contain metal halides such as ferric chloride, and ferric chloride mixed with sulfuric acid, or a halide, such as bromine as a solution of bromine and sulfuric acid or bromine in an organic solvent.

[0051] After the flakes are intercalated, any excess solution is drained from the flakes and the flakes are water-washed. The quantity of intercalation solution retained on the flakes after draining may range from 20 to 150 parts of solution by weight per 100 parts by weight of graphite flakes (pph) and more typically about 50 to 120 pph. Alternatively, the quantity of the intercalation solution may be limited to between 10 to 50 parts of solution per hundred parts of graphite by weight (pph) which permits the washing step to be eliminated as taught and described in U.S. Pat. No. 4,895,713, the disclosure of which is also herein incorporated by reference.

[0052] Referring now to FIG. 1, intercalated graphite flakes are advantageously exfoliated into flexible graphite particles by passing a stream of intercalated graphite flakes 2 through a flame 3 for only a few seconds at temperature up to or greater than 700° C., more typically 1000° C. or higher, to exfoliate, i.e. expand the particles, and a resulting stream of expanded graphite particles, or worms 5, are passed to the top 6 of a large open-topped vessel 7 into which the particles

fall freely and are randomly dispersed. From about 1-30% by weight of ceramic additives, indicated at 4, can be blended with the intercalated graphite flakes 2 to provide enhanced properties in the final flexible graphite product. The additives include ceramic fiber particles having a length of 0.15 to 1.5 millimeters. The width of the particles is suitably from 0.04 to 0.004 mm. The ceramic fiber particles are non-reactive and non-adhering to graphite and are stable at temperatures up to 2000° F, preferably 2500° F. Suitable ceramic fiber particles are formed of macerated quartz glass fibers, carbon and graphite fibers, zirconia, boron nitride, silicon carbide and magnesia fibers, naturally occurring mineral fibers such as calcium metasilicate fibers, calcium aluminum silicate fibers, aluminum oxide fibers and the like.

[0053] The dispersed expanded particles 5, with optional additive 4, are collected and confined in the large open-topped vessel as a layer 8 of pre-determined depth "d" and are to a large extent omnidirectionally oriented, with some horizontally aligned, as shown at 50 in FIG. 1(A), and many extending in other directions, including vertically as shown at 500 in FIG. 1(A), and in various directions other than vertical or horizontal as shown as 5000 in FIG. 1(A). The large open-topped vessel used to collect the omnidirectionally oriented particles can be in the form of a mold as shown at 7 shaped to receive a die 9 which is used to compress the layer 8 of omnidirectionally oriented exfoliated graphite particles 50, 500, 5000 to a density of from about 0.1 to 25 pounds per cubic foot at a thickness of from 25 to 0.15 inches. Under these conditions, the omnidirectional orientation of the exfoliated acid treated graphite is conserved to a substantial extent in the compressed planar flexible graphite article 100, having parallel opposed faces or major surfaces 101, 103, as shown in the sketch of the edge of the planar article illustrated in FIG. 2 and is also conserved when the material of FIG. 2 is pressed into sheet having a density of 25 to 100 pounds per cubic foot and a thickness of 0.15 to 0.04 inch as shown in the similar sketch of FIG. 2(A).

[0054] The use of continuous converging opposing belts, as shown at 457, 458 in FIG. 5, such as porous belts converging from a spacing of 25 inches to a spacing of 0.15 inch over a length of 8 to 12 feet, approximates the action of a mold and die with longer lengths, more than 8 feet providing increased conservation of omnidirectional orientation. A prior art highly densified sheet 200 of directly roll pressed intercalated acid treated graphite is illustrated in the sketch of FIG. 3 which shows the orientation of the exfoliated, expanded graphite particles 210 to be substantially parallel to the major opposed parallel surfaces 301, 303 of the planar sheet 200. FIG. 4 is a photograph of the edge of a compressed (100 lb./cu. ft.) planar article in accordance with the present invention corresponding generally to the sketch of FIG. 2 with the omnidirectionally oriented exfoliated, expanded graphite particles being correspondingly indicated at 50, 500, 5000.

[0055] The article of FIG. 3 is highly anisotropic with respect to thermal and electrical conductivity; the articles of FIGS. 2, 2(A) and 4 exhibit enhanced isotropy with respect to thermal and electrical conductivity, as compared to the article of FIG. 3.

[0056] The articles of FIGS. 2, 2(A) and the material shown in the photograph (100x) of FIG. 4 can be shown to

have increased thermal and electrical conductivity in the direction transverse to opposed planar surfaces 101, 103 as compared to the thermal and electrical conductivity in the direction transverse to surfaces 301, 303 of prior art material of FIG. 3 in which particles of expanded natural graphite unaligned with the opposed planar surfaces are not optically detectable.

[0057] With reference to FIG. 5, a system is disclosed for the continuous production of roll-pressed flexible graphite sheet. In the inventive system, graphite flakes and a liquid intercalating agent are charged into reactor 404. More particularly, a vessel 401 is provided for containing a liquid intercalating agent. Vessel 401, suitably made of stainless steel, can be continually replenished with liquid intercalant by way of conduit 406. Vessel 402 contains graphite flakes that, together with intercalating agents from vessel 401, are introduced into reactor 404. The respective rates of input into reactor 404 of intercalating agent and graphite flake are controlled, such as by valves 408, 407. Graphite flake in vessel 402 can be continually replenished by way of conduit 409. Additives, such as intercalation enhancers, e.g., trace acids, and organic chemicals may be added by way of dispenser 410 that is metered at its output by valve 411.

[0058] The graphite flakes in reactor vessel 404 are subjected to interlayer attack by the acid mixture intercalant, as described in U.S. Pat. No. 3,404,061 to Shane et al. The resulting intercalated graphite particles are soggy and acid coated and are conducted (such as via conduit 412) to a wash tank 414 where the particles are washed, advantageously with water which enters and exits wash tank 414 at 416, 418. The washed intercalated graphite flakes are then passed to drying chamber 422 such as through conduit 420. Additives such as buffers, antioxidants, pollution reducing chemicals can be added from vessel 419 to the flow of intercalated graphite flake for the purpose of modifying the surface chemistry of the exfoliate during expansion and use and modifying the gaseous emissions which cause the expansion.

[0059] The intercalated graphite flake is dried in dryer 422, preferably at temperatures of about 75 to about 150° C., generally avoiding any intumescence or expansion of the intercalated graphite flakes. After drying, the intercalated graphite flakes are fed as a stream into flame 300, by, for instance, being continually fed to collecting vessel 424 by way of conduit 426 and then fed as a stream into flame 300 in expansion vessel 428 as indicated at 2. Additives such as ceramic fiber particles formed of macerated quartz glass fibers, carbon and graphite fibers, zirconia, boron nitride, silicon carbide and magnesia fibers, naturally occurring mineral fibers such as calcium metasilicate fibers, calcium aluminum silicate fibers, aluminum oxide fibers and the like can be added from vessel 429 to the stream of intercalated graphite particles propelled by entrainment in a non-reactive gas introduced at 427.

[0060] The intercalated graphite particles 2, upon passage through flame 300 in expansion chamber 301, expand more than 80 times in the "c" direction and assume a "worm-like" expanded form; the additives introduced from 429 and blended with the stream of intercalated graphite particles are essentially unaffected by passage through the flame 300. The expanded graphite particles may pass through a gravity separator 430, in which heavy ash natural mineral particles

are separated from the expanded graphite particles, and then into a wide topped hopper 432. Separator 430 can be by-passed when not needed.

[0061] The expanded, i.e., exfoliated graphite particles fall freely in hopper 432 together with any additives, and are randomly dispersed and passed into compression station 436, such as through trough 434. Compression station 436 comprises opposed, converging, moving porous belts 457, 458 spaced apart to receive the exfoliated, expanded graphite particles 50, 500, 5000. Due to the decreasing space between opposed moving belts 457, 458, the exfoliated expanded graphite particles are compressed into a mat of flexible graphite, indicated at 448 having thickness of, e.g., from about 1.0 to 0.003, especially from about 1.0 to 0.1 inches, and a density of from about 5 to 125 lbs./ft<sup>3</sup>. Gas scrubber 449 may be used to remove and clean gases emanating from the expansion chamber 301 and hopper 432.

[0062] The mat 448 is passed through vessel 450 and is impregnated with liquid resin from spray nozzles 438, the resin advantageously being "pulled through the mat" by means of vacuum chamber 439 and the resin is thereafter preferably dried in dryer 460 reducing the tack of the resin and the resin impregnated mat 443 is thereafter densified into roll pressed flexible graphite sheet 447 in calender mill 470. Gases and fumes from vessel 450 and dryer 460 are preferably collected and cleaned in scrubber 465.

[0063] The calendered flexible graphite sheet 447 is passed through surface shaping unit 480 and is mechanically deformed at its surface by embossing die stamping or the like, and thereafter heated in oven 490 to cure the resin, to continuously provide a flexible graphite sheet 444 of repeated surface altered patterns such as the grooved patterns 600 shown in FIG. 5A, which can be cut to provide flexible graphite components 650 of a fuel cell such as fluid flow plate shown at 650 in FIG. 6A or gaskets 750 as shown at 700 in FIG. 5B.

[0064] Depending on the nature of the resin system employed, and especially the solvent type and level employed, a vaporization drying step may be included prior to the surface shaping (such as embossing) step. In this drying step, the resin impregnated flexible graphite sheet is exposed to heat to vaporize and thereby remove some or all of the solvent, without effecting cure of the resin system. In this way, blistering during the curing step, which can be caused by vaporization of solvent trapped within the sheet by the densification of the sheet during surface shaping, is avoided. The degree and time of heating will vary with the nature and amount of solvent, and is preferably at a temperature of at least about 90° C. and more preferably from about 90° C. to about 125° C. for about 3 to about 20 minutes for this purpose.

[0065] The above description is intended to enable the person skilled in the art to practice the invention. It is not intended to detail all of the possible variations and modifications which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such modifications and variations be included within the scope of the invention which is defined by the following claims. The claims are intended to cover the indicated elements and steps in any arrangement or sequence which is effective to meet the objectives intended for the invention, unless the context specifically indicates the contrary.

What is claimed is:

1. A graphite article comprising a flexible sheet of graphite having opposed generally planar major surfaces, the graphite sheet being formed of particles of exfoliated graphite, an optically detectable portion of said interlocked particles of expanded graphite being substantially unaligned with the opposed planar surfaces, the graphite sheet being characterized by having increased electrical and thermal conductivity in a direction transverse to the opposed planar surfaces as compared to a graphite sheet of the same thickness and density which does not comprise an optically detectable portion of particles of expanded graphite which are substantially unaligned with the opposed planar surfaces are not optically detectable.
2. The article of claim 1 wherein said optically detectable portion of said interlocked particles includes optically detectable particles that are transverse to the opposed parallel planar surfaces of the flexible graphite body.
3. The article of claim 2 having a thickness of from about 1.0 to 0.003 inch.
4. The article of claim 3 having a density of from about 5 to 125 pounds per cubic foot.
5. The article of claim 1 wherein ceramic fiber particles are admixed into the graphite sheet.
6. The article of claim 5 wherein the ceramic fiber particles have a length of about 0.15 to about 1.5 millimeters.
7. The article of claim 6 wherein the ceramic fiber particles are stable at temperatures up to about 2000° F.
8. An apparatus for the continuous production of resin-impregnated flexible graphite sheet, the apparatus comprising:
  - (i) a reactor vessel for containing as reactants graphite particles in mixture with a liquid intercalant solution to form intercalated graphite particles;
  - (ii) an expansion chamber in operative connection with the reactor vessel, the expansion chamber at a temperature of at least about 700° C., such that passing intercalated graphite particles from the reactor vessel to the expansion chamber causes expansion of the intercalated graphite particles to form exfoliated graphite particles;
  - (iii) a compression station positioned to receive exfoliated graphite particles for compressing such particles into a coherent self-supporting mat of flexible graphite;
  - (iv) an impregnation chamber for contacting the flexible graphite mat of (iii) with liquid resin and impregnating the mat with liquid resin;
  - (v) a calender mill disposed to receive the flexible graphite mat of (iv) for increasing the density of said flexible graphite mat to form a continuous flexible graphite sheet having a thickness of no more than about 1.0.
9. The apparatus of claim 8 which further comprises a device for mechanically deforming a surface of the continuous flexible graphite sheet of (v) to provide a series of repeating patterns on a surface of the flexible graphite sheet or the removal of material from the flexible graphite sheet in a series of repeating patterns.
10. The apparatus of claim 9 which further comprises an oven for receiving the mat from the device for mechanically deforming a surface of the continuous flexible graphite sheet to cure the resin with which the continuous flexible graphite sheet is impregnated.
11. The apparatus of claim 8 which further comprises a wash vessel containing water communicating with the reactor vessel to receive reaction product in the form of intercalated graphite particles from the reactor vessel and at least partially remove acid from the surface of the intercalated graphite particles.
12. The apparatus of claim 11 which further comprises a drying chamber for drying washed intercalated graphite particles.
13. The apparatus of claim 8 which further comprises a separator vessel interposed downstream from the expansion chamber to collect by gravity separation heavy solid mineral impurity particles.
14. The apparatus of claim 8 which further comprises a gas scrubber to collect gases generated in the expansion chamber.
15. The apparatus of claim 9 which further comprises a dryer to vaporize and thereby remove some or all of the solvent, without effecting cure of the resin system, prior to contacting the continuous flexible graphite sheet with the device for mechanically deforming a surface of the continuous flexible graphite sheet.
16. A system for the continuous production of surface patterned, resin-impregnated flexible graphite sheet containing resin and other additives which comprises:
  - (i) a reactor vessel for containing as reactants raw natural graphite flake-like particles in mixture with sulfuric and nitric acids;
  - (ii) an acid containing vessel communicating with said reactor vessel for the introduction of a mixture of sulfuric and nitric acid into said reactor vessel;
  - (iii) a graphite particle containing vessel for the introduction of graphite particles into the reactor vessel;
  - (iv) a first additive containing vessel communicating with said reactor vessel for the introduction of intercalation enhancing materials, acids or organic chemicals;
  - (v) a wash vessel containing water communicating with the reactor vessel to receive reaction product in the form of acid intercalated graphite particles and remove acid from the surface of the acid intercalated graphite particles and a portion of the mineral impurities contained in the natural graphite particles introduced into the reactor vessel;
  - (vi) a drying chamber for drying washed acid intercalated graphite particles;
  - (vii) conduit means extending from said wash vessel to said drying chamber for passing washed acid intercalated graphite particles from the wash vessel to the drying chamber;
  - (viii) a second additive containing vessel communicating with the conduit means of (vii) for adding pollution reducing chemicals to the washed, intercalated graphite particles to the washed acid intercalated graphite particles;
  - (ix) a collecting vessel for collecting washed acid intercalated graphite particles admixed with pollution reducing chemicals;

- (x) conduit means extending from said drying chamber to said collecting vessel for passing acid intercalated graphite particles admixed with acid additives from said drying chamber to said collecting vessel;
  - (xi) a third additive containing vessel communicating with said conduit of (x) for the introduction of ceramic fiber particles in the form of macerated quartz glass fibers, carbon and graphite fibers, zirconia, boron nitride, silicon carbide and magnesia fibers, naturally occurring mineral fibers such as calcium metasilicate fibers, calcium aluminum silicate fibers, aluminum oxide fibers and the like into said conduit and the admixing and entrainment thereof with acid intercalated graphite particles passing from the washing vessel to the drying chamber;
  - (xii) an expansion chamber enclosing an open flame at a temperature of 800 to 1300° C.;
  - (xiii) conduit means extending from said collecting vessel to said expansion chamber for passing dried acid intercalated graphite particles admixed with ceramic particles to said expansion chamber;
  - (xiv) gas inlet means communicating with the conduit means of (xii) for entraining the acid intercalated graphite particles admixed with ceramic particles in a stream of non-reactive gas and passing the entrained acid intercalated graphite particles admixed with ceramic particles into the open flame enclosed in said expansion chamber to cause expansion of the acid intercalated graphite particles of at least about 80 times to form vermicular elongated graphite particles;
  - (xv) a collecting hopper for receiving said vermicular elongated graphite particles admixed with ceramic particles;
  - (xvi) a separator vessel interposed between the expansion chamber and the collecting hopper to collect by gravity separation heavy solid mineral impurity particles from the mixture of vermicular graphite particles with ceramic particles;
  - (xvii) a gas scrubber communicating with said collecting hopper to collect gases generated in the expansion chamber;
  - (xviii) a compression chamber positioned to receive vermicular graphite particles mixed with ceramic fiber particles for compressing said vermicular particles mixed with ceramic particles into a coherent self-supporting mat of flexible graphite from about 1 to 0.015 inches in thickness and having a density of from about 5 to 25 lbs./ft.<sup>3</sup>;
  - (xix) an impregnation chamber for contacting the flexible graphite mat of (xviii) with liquid resin and impregnating said flexible graphite with liquid resin;
  - (xx) a dryer disposed to receive the impregnated flexible graphite mat of (xix) and heat and dry said mat;
  - (xxi) a calender mill disposed to receive the flexible graphite mat of (xix) for increasing the density of said flexible graphite mat to form a continuous flexible graphite sheet having a density of from about 5 to 80 lbs./ft.<sup>3</sup>, a thickness of from about 0.5 to 0.005 inches and evenly spaced apart opposite surfaces;
  - (xxii) a device for mechanically deforming a surface of the continuous flexible graphite sheet of (xxi) to provide a series of repeating patterns on said surface flexible graphite sheet or the removal of material from said flexible graphite sheet in a series of repeating patterns; and
  - (xxiii) an oven for receiving the mat from the dryer of (xxii) to cure the resin the mat.
17. A method for the continuous production of resin-impregnated flexible graphite sheet, the method comprising:
- (i) reacting raw natural graphite flake-like particles with a liquid intercalant solution to form intercalated graphite particles;
  - (ii) exposing the intercalated graphite particles to a temperature of at least about 700° C. to expand the intercalated graphite particles to form a stream of exfoliated graphite particles;
  - (iii) continuously compressing the stream of exfoliated graphite particles into a continuous coherent self-supporting mat of flexible graphite;
  - (iv) continuously contacting the flexible graphite mat with liquid resin and impregnating the mat with liquid resin; and
  - (v) continuously calendering the flexible graphite mat to increase the density thereof to form a continuous flexible graphite sheet having a thickness of no more than about 1.0 inches.
18. The method of claim 17 wherein wherein ceramic fiber particles are admixed with the intercalated graphite particles.
19. The method of claim 18 wherein the ceramic fiber particles have a length of about 0.15 to about 1.5 millimeters.
20. The method of claim 19 wherein the ceramic fiber particles are stable at temperatures up to about 2000° F.
21. The method of claim 17 which further comprises mechanically deforming a surface of the continuous flexible graphite sheet to provide a series of repeating patterns on a surface of the flexible graphite sheet or the removal of material from the flexible graphite sheet in a series of repeating patterns.
22. The method of claim 21 wherein the liquid resin is admixed with a solvent and the solvent is at least partially vaporized prior to mechanically deforming a surface of the continuous flexible graphite sheet.

\* \* \* \* \*